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CVI. *On the Capture of Electrons by Molecules.* By V. A. BAILEY, M.A., D.Phil.(Oxon), Associate Professor of Physics, University of Sydney, and J. D. MCGEE, M.Sc., Demonstrator in Physics, University of Sydney*.

1. **T**HE method of investigating the attachment of electrons to gas molecules which was described in a previous communication† has now been applied to the gases air‡, hydrogen chloride§ and ammonia¶.

The seemingly anomalous behaviour of electrons in the last gas and the consequent desirability of using an alternative method of study, provided an inducement for designing and constructing an instrument in which the length c of each of the two diffusion chambers can be varied without affecting the pressure and purity of the gas contained in the instrument.

As will be seen, this elaboration of the original instrument in which c was fixed, enables a notably simpler procedure to be followed in deducing the circumstances of the electrons' behaviour from the observations.

2. *Description of the Instrument.*

Most of the important features of the new instrument are represented in fig. 1, but for the sake of clearness in the

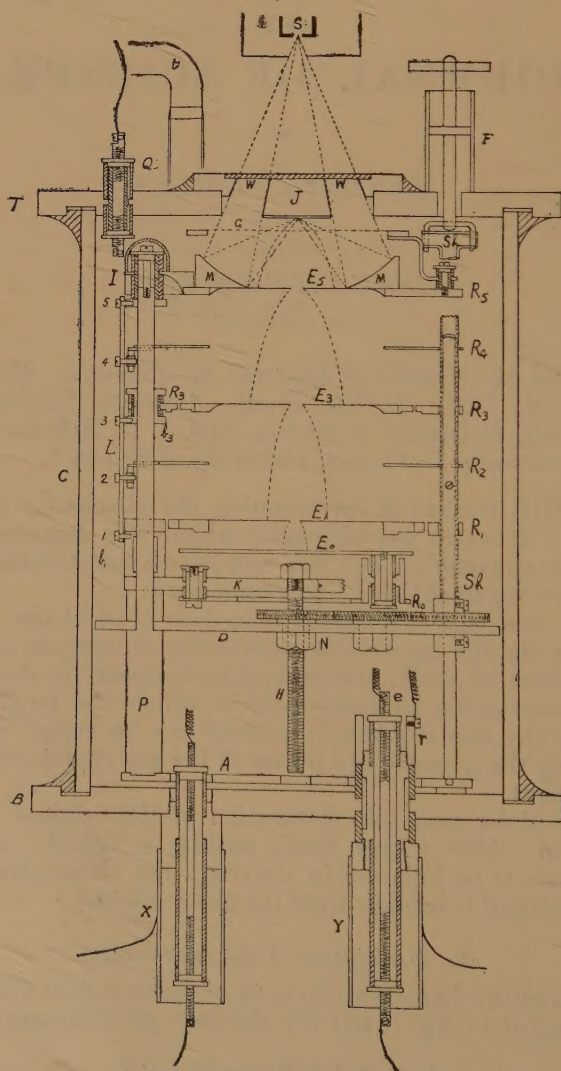
* Communicated by Prof. J. S. Townsend, F.R.S.

† V. A. Bailey, *Phil. Mag.*, Oct. 1925, p. 825.

‡ V. A. Bailey & A. J. Higgs, communicated to *Phil. Mag.* in July 1928.

diagram they are not all shown in their exact relative positions; the conducting parts are of either brass or phosphor-bronze, and the insulators of quartz or glass.

Fig. 1.



The plate B supports a glass cylinder C, insulated current leads like X and Y, and a disk A. Three parallel and

equidistant pillars, such as P, are fixed to the disks A and D, and to the ring R_5 by means of insulating systems like I.

Each pillar is fitted with brass bushes b_1 and b_3 , which enable the attached rings R_1 and R_3 to be moved vertically and not otherwise, R_3 being insulated from b_3 . A "lazy-tongs" system L is attached to each pillar by means of the pins 1, 3, and 5, which screw into b_1 , b_3 , and I respectively, these tongs carrying the rings R_2 and R_4 through pins 2 and 4 and tubular glass insulators. The bushes b_1 are also soldered to a plate K, shaped like an equiangular letter Y, which can be moved vertically by means of the rotation of a nut N acting on the rod H. This nut is turned by means of the shaft Sh through the gear-wheels shown, the shaft being engaged with a rod passing through the air-tight bearing F.

In this way the variable distances between the rings R_1 , R_2 , R_3 , R_4 , and R_5 are kept accurately equal.

Each of the electrodes E_1 and E_3 is supported and insulated from its ring R by three small quartz tubes, and each is connected to a rod e by a spiral spring of phosphor-bronze, its ring being connected to the corresponding guard-ring r .

The electrode E_0 is supported through insulators of tubular quartz by the ring R_0 , which in turn is insulated and supported from K.

A plate T rests upon C and carries four insulated leads Q, the quartz window W, the gas inlet-tube t , and the bearing F.

By suitably connecting the rings R and the gauze G to a battery of cells, a uniform electric field may be set up throughout the space between G and E_0 . The potential of T is adjusted so that an adequate stream of electrons passes through G towards the diffusion chambers, when ultra-violet light falls on the lower surface of the gold plate fixed to J. This light comes from a spark S through the window W, and is reflected on to J by the gold-plated annular spherical mirror M.

To reduce disturbance of the uniformity of the electric field by contact potentials, all the essential electrodes are gold-plated and polished.

The slits in E_5 , E_3 , and E_1 are respectively 1.5, 6.2, and 7.2 cm. long, and 4, 4.2, and 4.2 mm. wide. They were designed all to be 4 mm. wide, but the above errors in construction did not cause difficulty in the use of the instrument on account of the procedure followed with the experiments.

3. Theory of the New Method.

For the sake of convenience the relations established previously* are summarized here with the following notation:—

c = distance between successive slits, in cm.

p = pressure of gas, in mm. of mercury.

Z = electric intensity, in volts/cm.

S_1 = fraction of the stream approaching E_3 which passes through its slit.

S_2 = corresponding fraction for E_1 (S may be termed the distribution-ratio for its diffusion chamber).

R = the distribution-ratio with negative ions for either diffusion chamber.

k = mean energy of agitation of an electron in terms of the mean energy of agitation of a molecule at 15°C .

α = probability of attachment, of an electron to a molecule, per unit length of its motion in the direction of the field.

With the quantities c , p , and Z adjusted to known values, the ratios S_1 and S_2 are determined by measuring the mutual ratios of the currents i_0 , i_1 , and i_3 which arrive on E_0 , E_1 , and E_3 respectively. The normal distribution-ratio R can be determined as a known function of Z/c , either by calculation† or by experiments with pure hydrogen in the instrument; this function is represented by the curve in fig. 2.

S_1 and S_2 depend on three unknown quantities: k , α , and the electronic composition of the stream passing through the first slit; but the derived quantity

$$\alpha = S_1 \left(\frac{R - S_2}{R - S_1} \right)$$

is independent of the last factor, and can be expressed as a known function of k and α , namely:

$$\alpha = R(Z/kc)e^{-\alpha c} \dots \dots \dots (1)$$

To obtain another relation between k and α , the quantities

* *Loc. cit.*

$$\dagger R = \operatorname{erf}(v) - (1 - e^{-v^2}) / v\sqrt{\pi},$$

where $v = 1.34 \sqrt{Z/kc}$, and $k = 1$ for ions.

c , p , and Z are altered by the same factor n to the values nc , np , and nZ respectively, and the quantity a_n is determined experimentally as before. This gives

$$a_n = R(nZ/k.nc)e^{-na.nc},$$

since k and α/p depend only on the ratio Z/p ,

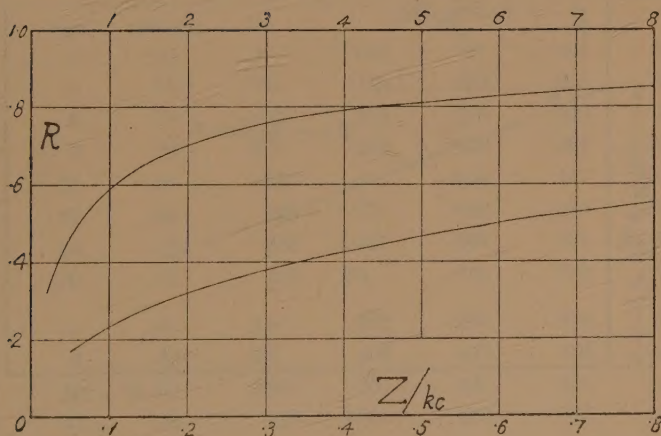
$$\therefore a_n = R(Z/kc)e^{-n^2\alpha c}. \quad (2)$$

From the simultaneous equations (1) and (2) we obtain

$$(n^2 - 1)\alpha c = \log_e (a/a_n),$$

$$R(Z/kc) = a^{\frac{n^2}{n^2-1}} / a_n^{\frac{1}{n^2-1}}.$$

Fig. 2.



The first of these gives the value of α , and the second, in combination with the curve in fig. 2, enables k to be determined.

But the following graphical method is to be preferred, for it supplies both a test of the theory and more accurate values of k and α .

Equation (2) may be expressed in the form :

$$y = -(\alpha c/2.3)x + (1 + \log_{10} R(Z/kc)),$$

where

$$x = n^2 \quad \text{and} \quad y = 1 + \log_{10} a_n.$$

So, if the values of y are determined experimentally for three or more values of x , and the points (x, y) are plotted,

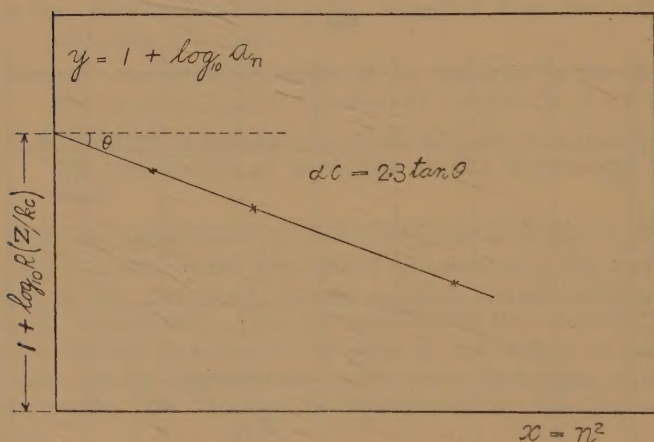
these should lie on a straight line whose slope gives $\alpha/2.3$ and whose intercept on the y -axis gives $1 + \log_{10} R(Z/kc)$, as illustrated in fig. 3.

When many determinations are to be made, it is convenient to evaluate k by the help of a curve derived from fig. 2, whose abscissæ represent Z/kc and ordinates $1 + \log_{10} R(Z/kc)$.

4. Experiments with H_2 .

As a test of the instrument, pure H_2 gas was introduced up to various pressures, and with different intensities the ratios S_1 and S_2 were obtained; these ratios correspond to

Fig. 3.



known values of Z/kc since k is now well established* for H_2 , so a comparison with the theoretical values of R obtained from fig. 2 is made in the last three columns of Table I.

In general there is good agreement between the values of S_1 , S_2 , and R for the same value of Z/kc , the small differences being due partly to errors in construction of the instrument and to the fact that in the calculation of R it is difficult to determine the effect of diffusion to the edges of the slits, which may be appreciable with widely-spreading streams.

S_1 is consistently from 2 to 3 per cent. less than S_2 , so the simple theory of the last section requires to be modified as follows:—To each diffusion chamber corresponds a different

* J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlii. (Dec. 1921).

normal distribution-ratio— R' for the upper, and R'' for the lower one. The quantity a is then given by

$$a = S_1 \left(\frac{R'' - S_2}{R' - S_1} \right),$$

and, in equations (1) and (2), R is replaced by R'' .

The numbers in the last three columns of Table I. show that for values of Z/kc greater than 0.75 the best values to adopt for R' are those given in the column under R , and for R'' the values of 1.02 R .

TABLE I.

<i>c.</i>	<i>p.</i>	<i>Z.</i>	<i>Z/p.</i>	<i>Z/kc.</i>	<i>S</i> ₁ .	<i>S</i> ₂ .	<i>R.</i>
cm.	mm.	volts/cm.					
4	2	10	5	·096	·197	·201	·228
4	4	10	2.5	·146	·252	·258	·277
4	8	10	1.25	·225	·319	·330	·336
4	8	20	2.5	·292	·359	·367	·377
4	16	20	1.25	·45	·434	·447	·448
4	32	20	·625	·75	·540	·548	·541
4	64	40	·625	1.537	·666	·689	·665
4	128	40	·312	2.8	·758	·780	·750
2	4	10	2.5	·292	·345	·353	·377
2	8	20	2.5	·585	·477	·486	·495
2	16	20	1.25	·90	·567	·571	·574
2	32	20	·625	1.50	·662	·672	·660

6. Experiments with NH_3 .

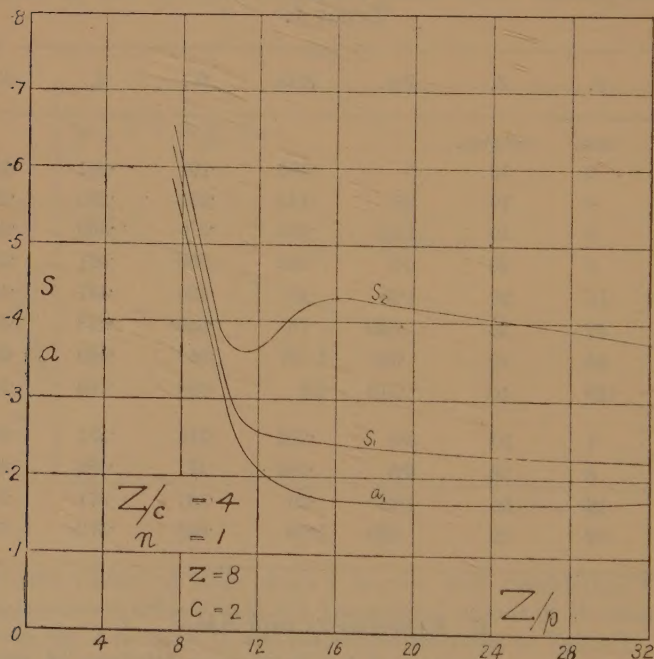
The gas was generated by heating a mixture of pure NH_4Cl and CaO in an evacuated flask to a temperature not exceeding $200^\circ C.$, and, after passing through a long tube packed with caustic potash, it was admitted to a freezing-trap, which was cooled to about $-78^\circ C.$ by a mixture of carbon dioxide snow and ether.

When about 4 litres had been so condensed, the freezing mixture was removed and part of the gas allowed to evaporate into a second trap, where it was similarly condensed. Without removing the freezing mixture the gas was then transferred by means of a mercury column pump to two flasks,

each of which contained a small quantity of anhydrous P_2O_5 , as supplied by Merck and Kahlbaum respectively.

A little later some liquid air was obtained, and this made possible a more effective fractional distillation of the remaining gas at lower temperatures. With this latter the pressure in the above two flasks was raised from 300 to 700 mm., and a third completely empty flask filled up to 700 mm. In order to obtain some information about the effect of the P_2O_5 on the gas in the first two, no drying agent was placed in the last flask.

Fig. 4 a.



During the first day there was a notable absorption of gas by the P_2O_5 , but the rate soon became small, and sufficient gas was left at the end of seven days to make all the observations required.

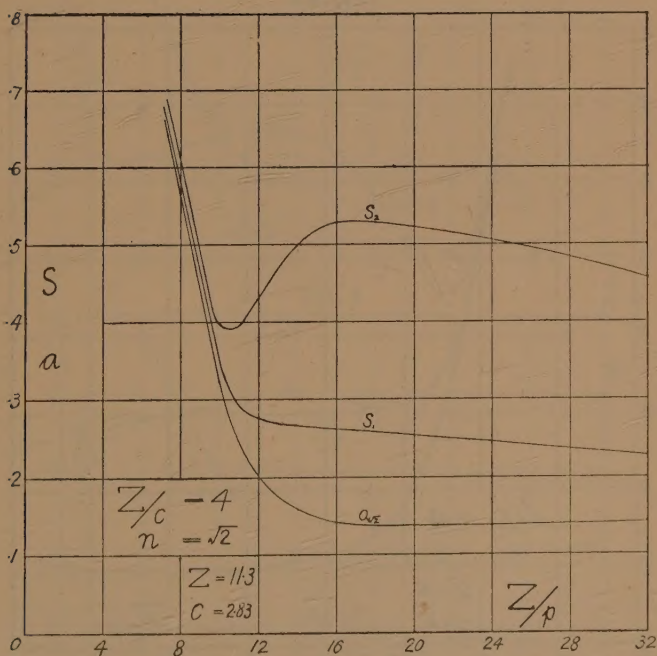
When the dry gas was admitted to the mercury gauges and diffusion instrument, it was found that the former were chiefly responsible for the loss of gas by adsorption, so the tap between the gauges and the instrument was turned off immediately after adjusting the gas-pressure, and after the observations the loss of gas in the gauges was restored

before this tap was turned again to verify that the gas in the instrument had not appreciably changed in pressure.

The first observations were made on a sample of gas from the flask which contained no drying agent, and as these were in substantial agreement with the results obtained for samples of NH_3 from the two flasks which contained P_2O_5 , the bulk of the work was carried out with the latter.

In general the electric intensity Z_g between the gauze G and the source of electrons J was kept approximately equal to the intensity Z of the uniform field extending between G

Fig. 4 b.



and E_0 , but at the higher pressures it required to be increased in order to maintain currents of magnitude sufficient for accurate measurements to be made. The possibility of this practice causing an error was examined by making observations with values of Z_g varying over a range so wide that the currents to the electrodes increased by a factor of about ten; c , p , and Z being kept unaltered.

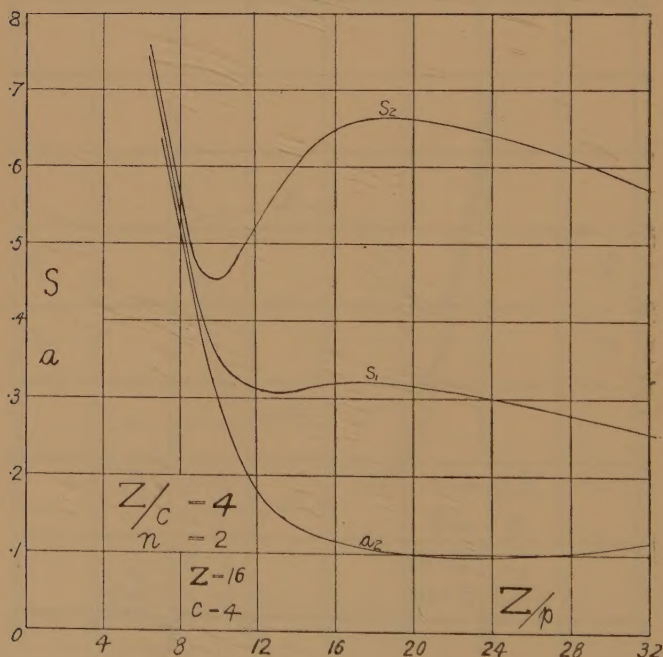
The ratios S_1 and S_2 varied with Z_g , but the quantity a calculated from their values remained constant within the limits of experimental error, which result is in agreement

with the theory, and also renders valid the method of securing convenient currents by variation of Z_p .

With the three variables c , p , and Z there are several ways of carrying out the work so as to apply the method described in Section 3, but the following plan was found to be the most convenient in practice :—

With the electric intensity Z and the chamber length c kept constant the pressure p was varied, and at the values 8, 10, 11.3, 14.1, 16, and 32 of the ratio Z/p the values of S_1 and S_2 were determined and plotted against Z/p , as shown

Fig. 4 c.



in fig. 4 a, which corresponds to $Z=8$ and $c=2$. Similar curves are obtained with Z and c both increased by a factor n , as shown in figs. 4 b and 4 c, which correspond respectively to the factors $\sqrt{2}$ and 2.

Since Z/c for all the observations has the same value 4, to which correspond $R'=.790$ and $R''=.810$ (from fig. 2), the values of a_n are given by

$$a_n = S_1 \left(\frac{.810 - S_2}{.790 - S_1} \right).$$

The numbers calculated in this way are represented by the lowest curve in figs. 4 *a*, 4 *b*, and 4 *c*.

It is evident from the curves for *S* that in the neighbourhood of the value 8 of *Z/p* there are very few ions present, and also that *k* must be increasing rapidly between the values 8 and 10. On the other hand, the striking increase of *S*₂, and the large separation of the *S*-curves between the

Fig. 5.

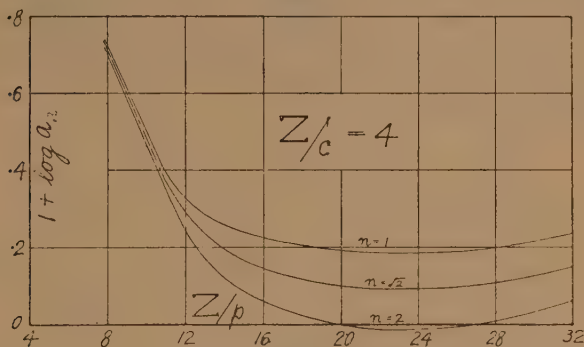
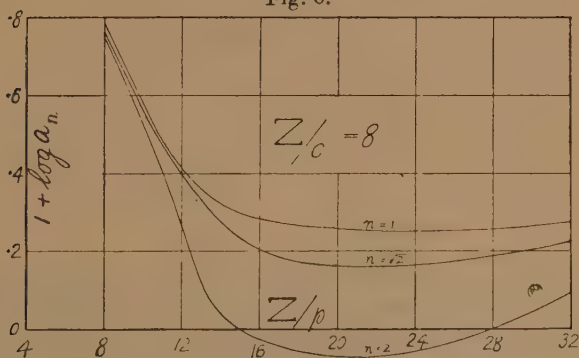


Fig. 6.



values 10 and 16 of *Z/p* indicate a rapidly increasing proportion of ions in the currents. For any given value of *Z/p* greater than 10 the curves for *S*₂, *S*₁, and *a* become further separated as *n* varies from 1 to 2, which is in accord with the conclusion that *α* increases with *p* if *Z/p* remains constant.

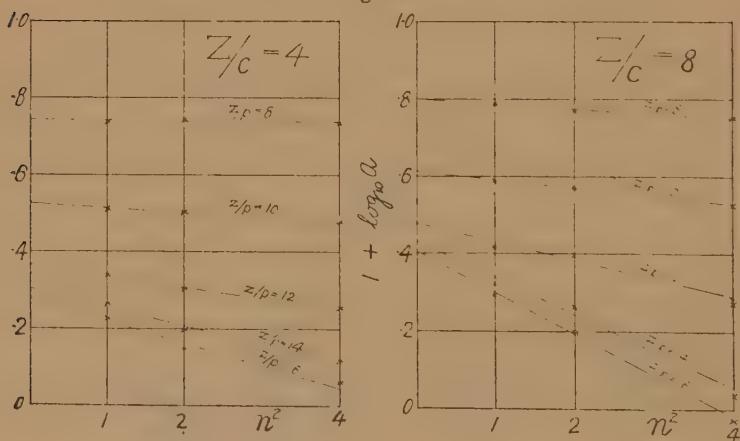
These inferences by inspection are completely confirmed by the quantitative determinations of *k* and *α* given below.

The values $1 + \log_{10} a_n$, obtained from the curves for *a_n*, are represented by curves in fig. 5, which thus correspond to $Z/c=4$.

In order to provide a further test of the reliability of these methods, another complete series of observations was obtained corresponding to $Z/c=8$; that is, curves were obtained similar to those shown in figs. 4*a*, 4*b*, and 4*c*, but with the values of Z fixed at 16, 22·6, and 32, and with pressures of the gas which were twice as large. To save space these are not given, but the corresponding curves for $1+\log_{10}a_n$ are shown in fig. 6.

With the help of the curves in fig. 5 (or fig. 6) the graphical method given in section 3, and illustrated by fig. 3, was now applied to the determination of the values of k and α corresponding to sets of experiments, the process being shown in fig. 7.

Fig. 7.



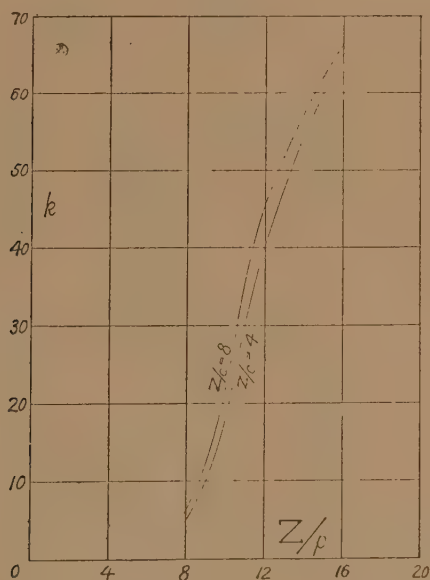
As an actual example we may consider the determinations for $Z/p=12$ with $Z/c=4$. From fig. 5, corresponding to $Z/p=12$, the values of $1+\log_{10}a_n$ are 3·40, 3·08, and 2·55 for $n=1$, $\sqrt{2}$, and 2 respectively. As shown in fig. 7, points are plotted with these for ordinates, and $n^2=1$, 2, and 4 respectively for abscissæ, and the straight line marked " $Z/p=12$ " is then drawn to lie evenly between the plotted points.

Since the slope of the line is ·0282, and c has the value 2, α must be given by $2·3 \times \cdot 0282/2$; that is, α is equal to ·0324; the value of p being $2 \times 4/12$, therefore $\alpha/p = \cdot 0486$.

The line cuts the vertical axis at ·367, which must then be the value of $1+\log_{10}R(Z/kc)$. This gives ·233 for $R(Z/kc)$, and thus with the assistance of fig. 2, k is found to be 40.

The values of k and α/p so determined are represented by curves in figs. 8 and 9. In each diagram there is good agreement between the curves obtained under the different conditions represented by the ratios Z/c , despite the facts which are now disclosed : that k and α/p change very rapidly with Z/p in the region under examination. This agreement, and the collinearity displayed in fig. 7 between the three points in each set, may be regarded as experimental confirmation of the theory in section 3, which is now seen to be applicable to NH_3 up to $Z/p=16$.

Fig. 8.



The effect of calculating the values of k by means of the distribution-ratios obtained with H_2 (section 4), instead of calculating by the curve in fig. 2, was to lessen the concordance between the upper parts of the two curves for k , but the results are not substantially different from those shown in fig. 8. The values of α , however, depend only on the upper parts of the distribution curves ($Z/kc > 75$), which agree well with the ratios obtained with H_2 .

For $Z/p=32$ there is some discordance between the results determined with the two different values of Z/c . The present theory may commence to become inapplicable to NH_3 in this region on account of the effects of ionization by collision of

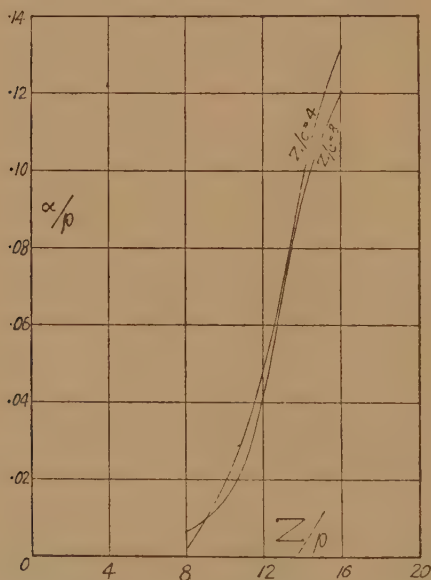
electrons with molecules, which are known to become appreciable in some gases under similar conditions; for example, in H_2O the current would increase by about 5 per cent. between successive slits with this value of Z/p and a pressure of 1 mm. So no deductions are made from the observations with $Z/p=32$.

5. Conclusions.

The probability h of attachment at a collision may be estimated by means of the formula *

$$h = 11 L^2 (\alpha/p) (Z/p) / k$$

Fig. 9.



if the mean free path L , of an electron at 1 mm. pressure of gas, be deduced from measurements of the viscosity of NH_3 . Accordingly, from Roth and Scheel's 'Konstanten der Atomphysik,' $L = 2 \times 10^{-2}$ cm.; and since from figs. 8 and 9 with $Z/p=12$, $k=43$, and $\alpha/p=.045$,

$$\therefore h = 5 \times 10^{-5} \quad \text{when} \quad k=43.$$

This method, however, is not a reliable one by which to examine the dependence of h on the energy k of the electron,

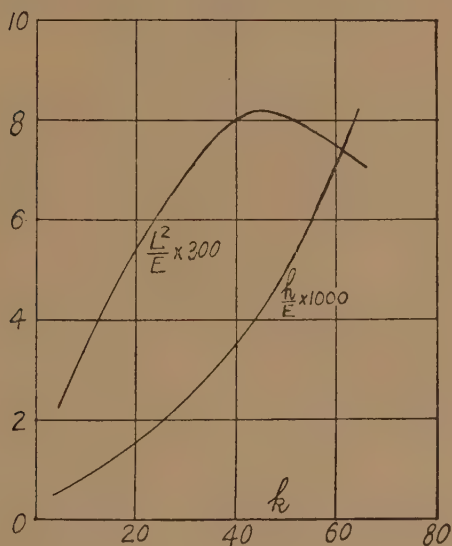
* Deduced from the relations $a = \hbar u / 1W$ and $W = .815 \text{ Ze} / mu$.

as it is known that L itself may vary considerably with k ; so the following argument is to be preferred :—

If E denote the energy (in volts) lost by an electron at a collision with a molecule, then for a given gas E is a function of k alone. The number ν of collisions made by an electron which travels 1 centimetre along the direction of the electric field, in the steady state of motion, is such that the work Z (volts) done by the field is equal to the energy lost in these collisions.

$$\therefore \quad \nu E = Z.$$

Fig. 10.



The probability of attachment in this distance is represented by α and also by νh .

$$\therefore \quad \nu h = \alpha;$$

$$\therefore \quad h/E = \alpha/Z = (\alpha/p)/(Z/p).$$

The values of h/E for different values of k may then be determined from the curves in figs. 8 and 9, and represented by a curve as in fig. 10.

This shows that as k increases from 5.5 to 64 the ratio h/E also steadily increases from 0.6×10^{-3} to 8.1×10^{-3} , *i. e.* by a factor of about 14.

It is easy to show that *

$$E = 7 \times 10^{-16} W^2 \text{ volts}$$

where W is the velocity of the stream of electrons in the direction of Z ; and as none of the many experiments made to date in different gases † has revealed an instance where W decreases as k increases, it may be concluded generally that E never diminishes as k increases ‡. It then follows that in NH_3 h increases by a factor not smaller than 14 when k varies from 5.5 to 64.

Some information concerning the variation of the mean free path L may be obtained in a similar way from a curve whose ordinates represent L^2/E , since it is easy to deduce from the above expressions for h and h/E that

$$L^2/E = k/11(Z/p)^2,$$

and so to determine this curve (fig. 10) by means of fig. 8.

This curve indicates that, as k increases from 5.5 to 45, the ratio L^2/E increases from 2.34 to 8.2, and as E is not diminishing, it follows that L^2 increases in this range by a factor of at least 3.5.

The conclusion that h may vary considerably with k in NH_3 and in air § makes it certain that the method used by L. B. Loeb || and H. B. Wahlin is liable in general to give erroneous results, for it depends on the assumption that h is a constant characteristic of the gas alone. There are other weaknesses in this method, some of which have already been pointed out ¶, so in referring to the table on p. 513 of his book, in which are given the values of $n(=1/h)$ obtained with this method, he states: "It is questionable whether the values are accurate in more than order of magnitude. They do differ, however, so widely in order of magnitude that even these crude early results give a good idea of n ." Further on he adds: "While these results are not of more than *qualitative* value. . . ."

We are inclined to doubt whether they even "give a good idea of n " on comparing Wahlin's value 10^{-8} for h in NH_3 with our lowest value, which is about 2×10^{-5} ; these are by

* J. S. Townsend and V. A. Bailey, *Phil. Mag.*, Nov. 1922, p. 1045.

† H_2 , O_2 , N_2 , He , A , Ne , CO , CO_2 , NO , N_2O , C_2H_4 , C_5H_{12} .

‡ The experiments of Townsend and Glasson, which might indicate the contrary, correspond to very different conditions, where the energies cause intense ionization by collisions.

§ V. A. Bailey, *loc. cit.*

|| L. B. Loeb, 'Kinetic Theory of Gases,' p. 510.

¶ V. A. Bailey, *Phil. Mag.*, July 1923.

no means of the same order of magnitude. To explain this discrepancy by assuming that our gas contained more of potent impurities than his, requires that ours should have contained a proportion of these at least 1000 times greater than did Wahlén's; there is, however, no reason to suppose that our samples of NH_3 were less pure than his. On the other hand, if it be argued that the disagreement is attributable to the difference in the energies of the electrons, then it has to be admitted that when the mean velocity of the electrons changes from 1.1×10^7 to about 2.6×10^7 cm./sec., the probability of attachment h increases by a factor of at least 1000; a change of such magnitude cannot be ignored, even if only "qualitative" results are sought. Since Loeb admits (p. 513) the greater reliability of the methods we have used, it would appear that the results obtained with his method, and set out in his table, may be quite misleading.

E. M. Wellish* has expressed the view that "an electron cannot effect a permanent union with an uncharged molecule to form a negative ion unless the relative velocity at collision exceed a critical value characteristic of the molecule concerned. . . . It is probable that the circumstances of an encounter as well as the relative velocity will determine the effectiveness of a collision so that only a fraction of these impacts will result in the formation of ions."

We are unable to see the necessity for his assumption of a minimum critical velocity, for the experimental facts he adduced in support of it can be understood from our point of view without requiring any additional hypothesis.

The NH_4Cl and CaO used was very kindly prepared for us by Mr. G. J. Burrows, of the Department of Chemistry.

We are also much indebted to the Colonial Sugar Refining Co., Ltd., for the supply of carbon-dioxide snow, and to the Commonwealth Oxygen & Accessories Co., Ltd., for the supply of liquid air, both without cost to the University.

It is to be hoped that their example will find imitators in Australia, where the policy adopted with striking success by the industries of other countries, of assisting research in pure and applied science, is still somewhat disregarded.

In conclusion we desire to record our appreciation of the skill and resource shown by Messrs. G. C. Barnes and H. Taylor in the construction of the apparatus used in this work.

* E. M. Wellish, *Am. Journ. Sci.* xliv. p. 26 (July 1917).

CVII. *Spark Ignition.* By E. TAYLOR JONES, D.Sc.,
*Professor of Natural Philosophy in the University of
 Glasgow*.*

[Plates XXI. & XXII.]

THE substance of the following communication was contained in a lecture to Section A of the British Association at Glasgow on September 10th, 1928. The chief topics discussed are the nature of the action of an electric spark in producing ignition of an inflammable gaseous mixture, and the conditions which determine whether a spark will or will not ignite a given mixture.

One of the earliest experimental results published on this subject was the observation by Thornton† that the heat dissipated in a spark just sufficient to cause ignition is less if the spark is produced by the discharge of a condenser than if it is produced (as in “low tension” or “inductance” sparks) by separating the electrodes from contact so as to interrupt a current in an inductive circuit. An explanation of this result, based on the view that spark ignition depends upon the volume of the gas which the spark can by its own heat raise to the ignition temperature‡, was suggested by Taylor Jones, Morgan, and Wheeler§. A condenser spark of very short length between metal points being regarded as an instantaneous point source of heat in a uniform medium, the temperature θ in its neighbourhood is represented by Fourier’s expression

$$\theta = \frac{Qe^{-r^2/4kt}}{8c(\pi kt)^{3/2}}, \quad \dots \dots \dots (1)$$

* Communicated by the Author.

† Phil. Mag., November 1914.

‡ See Wheeler, Trans. Chem. Soc. cxvii. p. 903 (1920); also the ‘Third Report of the Explosions in Mines Committee of the Home Office,’ 1913. The argument for this view may be stated as follows:—If we suppose that a small spherical volume of the gas is heated by the spark to the ignition temperature, the gas within this volume is burnt, and its temperature is raised further by the heat resulting from the chemical action. At the surface of the sphere there will, therefore, be a large temperature gradient and rapid loss of heat by conduction. The rate of cooling of the sphere due to this cause is proportional to the ratio of its surface to its volume, and is very great if the sphere is very small. Consequently the small flame started in the sphere will soon become extinguished by the conduction from its surface, and will therefore fail to spread throughout the gas, unless the volume of the sphere exceeds a certain minimum value.

§ Phil. Mag., February 1922.

in which Q is the quantity of heat dissipated in the spark, k is the thermometric conductivity, and c the thermal capacity per unit volume of the gas (supposed uniform), r is the distance from the source, and t is the time after the moment at which the heat is communicated. If an inductance spark be regarded as a source in which the heat is supplied to the gas at a uniform rate over an interval of time T , the temperature distribution may be deduced from (1) by integration. In the paper cited the results of numerical calculations based upon (1) were given, which showed that in the case considered the volume of the spherical portion of the gas, the boundary of which was just raised to a certain temperature, was greater in the case of the instantaneous source than in that of a source in which the heat supply was continued at a uniform rate for a finite interval of time, the total heat supplied being the same in both cases*.

The general proof that this result holds also for a point source in which the heat Q is supplied over a finite interval of time, whether uniformly or not, may be arrived at in the following manner:—In fig. 1 let curve A† represent the form of the temperature wave (θ, t) at any distance r from an instantaneous point source. The temperature at this distance rises rapidly to a maximum and falls more slowly from it. The maximum temperature is attained at the time $t=r^2/6k$, and is higher the shorter the distance r from the source, being, in fact, inversely proportional to the cube of the distance from the source, as may be seen by substituting this value for t in (1).

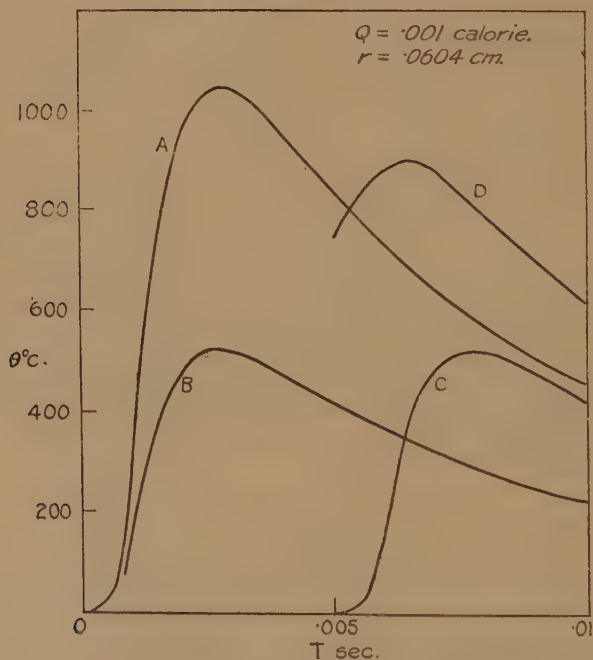
If we now suppose that the heat Q is communicated in two equal parts at an interval of time T (represented in fig. 1 by 0.005 sec.), the temperature at the same distance is given by the sum of the ordinates of the two curves B and C, each of which has one-half the amplitude of A. The maximum in the resultant curve occurs at a time shortly before the maximum of the second component, and it is evident that the resultant maximum is smaller than the sum of the maxima of the two components, and therefore than the maximum of

* Coward and Meiter have recently (Journ. Amer. Chem. Soc. xlix. p. 396, 1927) determined experimentally the least volume which must be heated, by a condenser spark in a methane-air mixture, to the ignition temperature in order to ensure general inflammation, and found that the volume is of the same order of magnitude as that calculated from the expression (1).

† Curve A in fig. 1 is calculated from the expression (1) with $Q=0.001$ calorie, $r=0.0604$ cm., $k=0.2188$, $c=0.00032$. The maximum temperature is 1044° C. at $t=0.002779$ second.

the original curve A. The resultant maximum also evidently diminishes as the interval of time between the two components increases. We may conclude that the result of dividing the heat supplied into two equal instalments separated by any finite interval of time is to lower the maximum temperature at any given point in the neighbourhood. Similar considerations show that the same result holds if the two instalments are unequal, also if the heat is divided into three or more instalments, equal or unequal,

Fig. 1.



supplied at equal or unequal intervals of time. The limiting case of a continued source, *i.e.*, a very large number of infinitesimal instalments following one another at infinitely short intervals of time, is also included. Curve D in fig. 1 shows a portion of the temperature wave at the same distance from a point source of the same total heat, but in which the heat supply is continued uniformly for 0.005 second.

The general result may be stated as follows:—If a given quantity of heat is supplied at a point of a uniform conducting medium in any manner during a finite interval of

time, the maximum temperature at any neighbouring point is lower than it would have been if the heat had been supplied all at the same instant.

By considering the distance from the source at which the temperature just rises to a given value, instead of the maximum temperature at a given distance, we arrive at the following corollary to the above theorem:—If a given quantity of heat is supplied at a point of a uniform conducting medium in any manner during a finite interval of time, the volume of the medium, the boundary of which is just raised to any given temperature, is smaller than it would have been if the heat had been supplied all at the same instant. This follows from the theorem and the result, previously stated, that for instantaneous sources the maximum temperature diminishes with increasing distance from the source.

The introduction of “volume” instead of “distance” in the corollary follows from the assumed uniformity of flow of heat in all directions. Since, however, the proof of the theorem does not depend upon the precise form of curve A in fig. 1, the theorem and its corollary are applicable to the case of a point source in a conducting medium between two plane parallel non-conducting walls at a short distance apart, or to that of a point source in a thin column of conducting material bounded laterally by non-conductors. If in these cases the bounding walls were made conducting some of the heat would enter the walls and would thus be lost to the medium between them, but since there seems to be no reason for supposing that the medium would lose more heat in this way with the instantaneous source than with the divided or continuous source, we may assume the theorem and its corollary to hold also in this case.

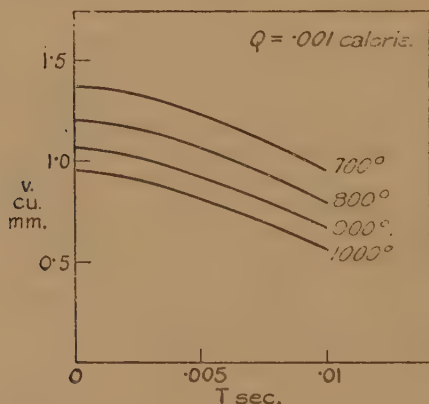
The magnitude of the effect of the duration of the heat supply is illustrated by the curves in fig. 2, in which the ordinate represents the volume of gas, the boundary of which is just raised to a definite temperature by a point source of heat continued at a uniform rate for a time T represented by the abscissa. The volumes are calculated, from the integral of the expression (1) *, for four temperatures (within the range of the ignition temperatures of methane-air mixtures), the values assumed for the constants being those given in the second footnote on p. 1091. It will be seen that the volume is greatest for an instantaneous source ($T=0$), and that it diminishes steadily as the duration of the heat supply is

* See Phil. Mag. p. 364, February 1922.

increased. The same holds when the heat supply, instead of being continued uniformly for time T , is divided into a given number of equal instalments supplied at equal intervals over this time. It is the increase in the total duration of the heat supply, rather than an increase in the number of instalments, which causes the reduction in the volume raised to the given temperature. An increase in the number of instalments (supposed equal and equally spaced in time), without increase in the total duration, has the opposite effect.

According to the hypothesis that ignition depends upon the volume of the gas which is raised to the ignition temperature, it follows from the corollary stated above that an instantaneous point source of heat is more effective in ignition than

Fig. 2.



a point source in which the heat is supplied in any manner (continuous or discontinuous) over a finite interval of time.

Experimentally it is easy to produce sources of approximately the same total heat, but having different time distributions, by connecting a condenser of variable capacity to the electrodes of a spark-gap connected with the secondary of an induction coil fed with a primary current which has a constant value at the moment of break. With a large value of the secondary capacity a single spark is obtained, and as the capacity is diminished the discharge produced by each interruption of the primary current divides into two, three, or more sparks. When the secondary condenser is disconnected we have the ordinary induction coil discharge consisting of a preliminary spark followed by a continuous but pulsating and decaying arc.

In fig. 3 (Pl. XXI.) are shown six induction coil spark discharges produced in this way, between the ends of two wires at a very short distant apart, and photographed with the aid of a rotating mirror. That the energy dissipated in the six discharges was approximately the same is a consequence of the fact that the primary current at break, and therefore the energy supplied to the system, was the same in all. Calorimeter measurements of the heat of the sparks in such experiments also show that it is practically independent of the secondary capacity*.

An experiment described by Morgan† shows that the effectiveness of a magneto spark in ignition increases with the capacity of a condenser connected with the spark-gap electrodes. This result is in agreement with the theoretical views described above, since the total duration of the discharge in general diminishes as the secondary capacity is increased (see fig. 3, Pl. XXI.).

A simple form of explosion vessel which the present writer has found suitable for illustrative experiments on spark ignition consists of a strong glass tube of uniform bore, about 16 inches long and $1\frac{1}{4}$ inches internal diameter, slightly constricted at the upper end in order to hold firmly a plug of insulating material which closes the tube at this end and carries a gas inlet-tube and the electrodes of an adjustable spark-gap. A piston of felt, movable easily in the glass cylinder, is fitted to the end of a long brass tube of $\frac{1}{4}$ in. diameter which acts as air inlet. The glass cylinder is fixed firmly in a vertical position, the brass tube passing through a guide about 2 inches below the lower end of the cylinder. The upper surface of the guide also acts as a buffer from which the piston rebounds after the explosion. A scale of inches runs along the length of the cylinder, to measure the air introduced, the uppermost inch being divided into tenths for the measurement of the volume of gas admitted‡. A magneto (or an induction coil) and a condenser connected with the spark electrodes complete the apparatus. The piston is first set at a suitable mark near the top of the cylinder, gas is admitted for a short time and is then cut off

* A form of calorimeter suitable for comparative measurements of the heat of sparks consists of a gas thermometer the bulb of which contains the spark-gap. The deflexion of the liquid column produced by a series of sparks, and measured from the zero observed after sparking has ceased, gives a measure of the heat produced in the sparks.

+ 'Electric Spark Ignition,' pp. 31, 32 (1920); 'Engineering,' Nov. 3, 1916.

‡ Explosion tubes of this form were used for illustrating the lecture in Glasgow.

by a stopcock in the gas inlet-tube. The piston is drawn down to a suitable distance (depending upon the strength of mixture required) and a stopcock near the lower end of the air inlet-tube is then closed. A half turn of the magneto armature (giving one break of the primary circuit) produces the spark, and if the mixture is such that an explosion of sufficient violence results, the piston is blown out of the cylinder and after the rebound re-enters the cylinder to a certain distance. A scale of tenths of an inch may be marked on the cylinder at the lower end to indicate this distance, which gives a measure of the impulse of the explosion*.

By means of this apparatus the igniting action of sparks of different kinds between electrodes of different forms can be conveniently studied, and the superiority of a condenser spark over the ordinary magneto spark (*e.g.*, with pointed electrodes of steel or tungsten), indicated by the above theory, can easily be demonstrated.

Ignition by Short Sparks between Spherical Electrodes.

When ignition experiments are tried with short sparks between spherical electrodes of metal †, a number of results are found which appear, at first sight, to be contrary to the thermal theory. In the first place ignition is difficult and very erratic unless the metal surfaces are clean. It is scarcely to be expected, however, that the loss of heat which undoubtedly takes place by conduction from the gas to the electrodes would be less when these are clean than when they are covered with a layer of oxide or other substance of smaller conductivity than the metal. The result, therefore, seems to point to some action other than thermal as the cause of ignition. Further, when different metals are used as electrodes the igniting effect does not seem to depend appreciably upon their thermal conductivity. In making this comparison care should be taken to use electrodes of the same curvature (since the igniting power of the spark increases with their curvature), and they should be well cleaned before the experiment. In this way curved surfaces of copper, steel, and zinc were found to be equally effective in ignition, *i.e.*, to be just capable of igniting a given

* The pressure developed in an explosion is usually independent of the nature and intensity of the spark, so long as the spark is sufficient to produce an explosion at all (see Morgan, 'Electric Spark Ignition,' p. 15).

† Short cylinders of about 8 mm. diameter, having spherical ends of about 1 cm. radius of curvature, and placed so as to form a gap 0.15 mm. wide at its narrowest part, were used in most of the experiments described in this section.

mixture when the sparks were of the same kind and length, and were produced by the interruption of the same primary current. Of the metals examined (copper, steel, zinc, platinum, lead) lead was found to be the most suitable for ignition experiments; the surface of this metal is less easily spoilt by the tarnishing due to the sparks or to the flame. Carbon electrodes, though not so effective in ignition as those of clean lead, are also suitable because they do not require to be cleaned as do metallic surfaces.

Another result which appears to be contrary to the thermal theory is found when the effect of connecting a condenser to the spherical electrodes is examined. With electrodes and gap of the dimensions stated above, the effect of the condenser is exactly opposite to that observed when pointed electrodes are used. The condenser produces a decided diminution in the igniting power of the spark, and the inferiority of the condenser spark with the spherical electrodes is quite as marked as its superiority when the electrodes are metal points. In one experiment, with spherical carbon electrodes, ignition without the condenser occurred at a primary current of 0.7 ampere; with the condenser ignition failed at 10 amperes, *i. e.*, with a spark of nearly 200 times as much energy.

This result is directly contrary to that derived from the theory of thermal conduction from point sources, and we must conclude either that the thermal theory is wrong, or that some other action takes place, when spherical electrodes are employed, which is of such greater influence in ignition than thermal conduction as to mask its effect.

For the further investigation of this matter some photographs of the sparks between spherical electrodes were taken, six specimens of which are shown in fig. 4 (Pl. XXI.). These sparks were produced, by a magneto, between lead cylinders 8 mm. in diameter, the spherical ends of which were set at 0.15 mm. apart. The camera used in photographing them had a quartz lens of 15.6 cm. focal length, the linear magnification being 1.5 cm. The sparks shown in fig. 4 (Pl. XXI.) are "ordinary" magneto sparks, no condenser being connected with the electrodes.

An examination of fig. 4 (Pl. XXI.) shows that the ordinary spark between spherical electrodes differs in one important particular from the usual short spark which we have regarded as a point source. The discharge begins at the centre (*i. e.*, the narrowest part) of the gap, but some portion of it spreads towards the sides, and in spreading it lengthens so that it can no longer be regarded as even approximately a

point source*. The spreading of the discharge over the surfaces of the electrodes does not occur when a condenser of considerable capacity is connected with them. In fig. 5 (Pl. XXI.) are shown seven induction-coil sparks between the lead cylinders, the gap in each case being placed centrally just above a Meker burner †. The first five passed while a condenser was connected with the terminals; they show no spreading and they failed to produce ignition ‡. The sixth and seventh sparks were produced after the condenser was disconnected; of these the sixth shows spreading and produced ignition, the seventh shows no spreading and failed to ignite. The primary current interrupted was the same in all seven.

In fig. 6 (Pl. XXII.) are shown seven magneto sparks between spherical electrodes of platinum. Of the seven only the second and the fifth show evidence of spreading, and only these two produced ignition.

The conclusions to be drawn from an examination of these photographs, and a number of others of a similar kind which were taken, are that, in the case of short sparks between spherical electrodes of metal or of carbon:

- (1) the ordinary high-tension discharge (without secondary condenser) tends to spread from the centre towards the sides of the gap when the electrodes are of carbon or of clean metal;
- (2) the tendency to spread increases with the primary current;
- (3) the spreading does not occur, or occurs much less readily, over metal surfaces which are not clean;
- (4) ignition does not occur, or occurs only with great difficulty, unless the discharge spreads;
- (5) ignition does not always occur if there is spreading.
- (6) spreading does not occur if a condenser of considerable capacity § is connected with the electrodes.

* That the spreading is not an effect caused by gaseous combustion is shown by the fact that the discharges in fig. 4 (Pl. XXI.) took place in ordinary air free from inflammable gas.

† Ignition experiments with a burner may be made either while the gas is flowing or in the still gas which remains above the burner for a short time after the gas is turned off. A large Meker burner is the most suitable for the purpose.

‡ Owing to the much greater brightness of the condenser sparks the aperture of the lens was reduced to its minimum for the first five sparks. Their images are, however, still rather enlarged by halation.

§ The capacity must be sufficiently large to prevent the formation of an arc instead of a single or multiple spark (see the author's 'Theory of the Induction Coil,' p. 151).

With these facts in mind it is easy to understand why the ordinary spark is a better igniter than the condenser spark when spherical electrodes are used. The ordinary discharge, in spreading to the outer and wider parts of the gap, is able to warm the requisite volume of gas to the ignition temperature, not by thermal conduction but by its own expansion. The condenser spark, on the other hand, being confined to the narrowest part of the gap, can warm the surrounding gas only by conduction*. It is true that in the case of the ordinary spark between spherical electrodes, only a fraction of the heat is actually utilized in producing ignition, viz., the heat of that portion of the discharge which is near the edge of the gap. It is quite in accordance with the thermal theory, however, that an enlarged source may be a better igniter than a point source of greater heat. For the distribution of temperature round an instantaneous point source at any time after the heat is communicated is such that the temperature is highest in the position of the source, and falls off in all directions from this point. If the boundary of a certain volume of the gas is at the ignition temperature, the inner portions of this volume must be at a temperature above this, and therefore at an unnecessarily high temperature for the production of ignition. It is clear that, in regard to the volume raised to the ignition temperature, a better distribution would be one in which the heat is more evenly distributed, so that the temperature throughout this volume is uniform. An instantaneous point source, though superior to a continued point source, is inferior to an enlarged source of the same or even less total heat.

It appears, therefore, that the results, both with pointed and with spherical electrodes, are consistent with the view that the most effective spark in ignition is that which heats the greatest volume of the gas to the ignition temperature. With pointed electrodes the heating is effected by thermal conduction from the source, with spherical electrodes by expansion of the source itself.

Some further points now remain to be considered in regard to the discharge between spherical electrodes. The horizontal striations which appear in the photograph of the spreading discharge in fig. 5 (Pl. XXI.), and less clearly in

* It might be expected that the condenser spark, being in the position in which it can give heat most readily to the electrodes, would communicate less heat to the gas than would the ordinary spark. Calorimeter experiments, however, with small spherical electrodes of carbon, indicated that the gas receives slightly more heat from condenser sparks than from ordinary sparks produced with the same primary current.

figs. 4 and 6 (Pls. XXI. & XXII.), suggest that the apparent spreading is a radial movement, or wandering, of the arc portion of the discharge, the striations corresponding to the oscillations of the induction coil or magneto system*. That this is the case is confirmed by photographs of the discharge taken with the help of a rotating concave mirror, some of which are reproduced in fig. 7 (Pl. XXII.). They show a number of spark discharges, produced by an induction coil without secondary condenser, between spherical electrodes of carbon. Nearly all the images show the wandering of the arc, the movement being upwards, or downwards, or along other radii. Frequently the arc wanders to the edge of the gap and breaks off there, the discharge then beginning again at the centre, sometimes afterwards wandering along a different radius, as in the fourth, fifth, and sixth images. This is the explanation of the fact that in several of the camera photographs (*e. g.*, the first in fig. 4, Pl. XXI.) the "spreading" appears to take place both upwards and downwards in the same discharge. None of the lines in fig. 7 (Pl. XXII.) show any bifurcation, the discharge passing at only one part of the gap at a time. The curvature of the lines during wandering shows that the speed of the lateral movement of the discharge is greatest at the centre of the gap, which is to be expected since the radial variation of the width of the gap is here smallest†.

With regard to the influence of the wandering on ignition, it is probable that the most effective discharges in this respect are those in which the arc wanders to the edge of the gap and remains there for an appreciable time, as in the sixth and thirteenth images in fig. 7 (Pl. XXII.). On several occasions it was observed that a discharge which broke off just after reaching the edge, to recommence at the centre, was incapable of producing ignition. In such cases it must be concluded that though the wandering is accompanied by a sufficient enlargement of the source, the time for which the enlargement endures is too short to result in ignition‡.

The wandering of the arc takes place less readily when the width of the gap is increased. Consequently it might be expected that within certain limits a narrow gap between

* See 'The Theory of the Induction Coil,' fig. 61, p. 147, and fig. 93, p. 201.

† The photographs in fig. 7 (Pl. XXII.) suggest that the wandering is accompanied by an increase of width, as well as an increase of length, of the arc.

‡ The whole time of duration of each of the discharges shown in fig. 7 (Pl. XXII.) was about 1/100 second.

spherical electrodes would be more effective in ignition than a wider one. This was found to be the case with the carbon spherical electrodes used in the present experiments. The igniting effect of the spark was distinctly better when they were 0.15 mm. than when they were 0.3 apart, the heat of the spark being practically the same on both occasions. The greater ease of wandering in the narrower gap was more effective than the greater length of the initial spark in the wider one*.

The wandering also depends upon the curvature of the electrodes, and in the case of sharply-pointed electrodes it must be greatly restricted by the fact that here any lateral movement of the arc would be accompanied by excessive increase of length. The possibility suggested itself, however, that some slight effect of wandering might be observable with pointed electrodes if these were of the most suitable material. When ignition was tried with a very short spark between carbon points it was found that the addition of a secondary condenser now produced no improvement. Ignition was effected with equal success whether the condenser was connected or not. The same was found with pointed electrodes of clean lead. In these circumstances the slight wandering over the sides of the electrodes in the case of the ordinary spark apparently produces as much effect in ignition as the superior temperature distribution due to thermal condition in that of the condenser spark.

As to the cause of the wandering of the arc, this cannot be traced to the action of thermal convection arising from the heating of the gas by the initial spark. The photographs in figs. 4 and 7 (Pls. XXI. & XXII.) show that the movement of the arc is as often downwards as upwards. Nor can the wandering be attributed to thermionic action, since the movement is from the centre towards the outer portions of the gap where the surfaces of the electrodes are cooler. The wandering must be attributed to some property of the surfaces which is independent of thermal action. Now it is an observed fact that the wandering takes place much less readily if the electrode surfaces are not clean or are tarnished, and this fact suggests that photoelectric action plays a part in determining the position of the arc. We may suppose that the electrode surfaces at the centre are to some extent "spoilt" by the initial spark, so that the arc

* The condenser spark between spherical electrodes, in which there is no wandering, conforms to the general rule that the igniting power increases with the width of the gap

which follows it passes more readily across a neighbouring part of the gap where the surfaces are cleaner. The wandering of the arc thus represents the tendency of the arc to pass across parts of the gap where the surfaces have not been spoilt by the previous portions of the discharge. According to this view of the matter the direction of the wandering, which is apparently quite capricious, is that along which the surfaces at the time are cleanest, and where the easiest path is prepared for the discharge by photo-electric action.

That the wandering does not occur with condenser sparks is accounted for by the fact that it is a comparatively slow movement, and that it requires a much longer time to develop than that occupied by a single condenser spark. In fig. 8 (Pl. XXII.) are shown rotating-mirror photographs of four multiple spark discharges produced between the carbon spherical electrodes by an induction coil with secondary condenser. The capacity of the condenser was considerably less than the maximum which allowed sparks to pass, so that each discharge consisted of a large number of separate sparks. Each spark appears at the centre of the gap, and no part of the discharge shows any tendency to wander towards the side.

In connexion with the question of the condition requisite for ignition there is another point to which reference should be made here. Observers whose experiments on ignition by electric sparks or other forms of electric discharge have led them to conclude that ignition is not due to any thermal action of the current, have sometimes suggested that the current itself (or the ionization) in the gas is the determining factor in ignition. It is not difficult to show, however, that in the present experiments with spherical electrodes the maximum current crossing the spark gap is much greater in the case of the condenser spark than in that of the ordinary spark, though the latter is, as we have seen, much the better igniter. Let us suppose that a condenser of capacity C is connected with the electrodes, so that the discharge takes the form of a single spark in which the current oscillates with high frequency n , determined by the capacity C , and the self-inductance of the short wires by which it is connected to the electrodes. Then if the sparking potential is V_0 , the maximum value of the current in these oscillations is (if we neglect damping) $2\pi n C V_0$. In the present experiments V_0 was about 1000 volts, C about 0.004 microfarad, and n was not less than

10^6 per second. Consequently the maximum current in the condenser spark was, at a low estimate, 25 amperes.

When the condenser is replaced by one of very small capacity, the discharge changes into a spark of the ordinary kind, consisting of an initial capacity portion followed by a pulsating and decaying arc. The maximum current in the capacity portion is given by the same expression with the appropriate values of n and C , and since n is inversely proportioned to \sqrt{C} , the maximum current is now considerably less than before, being directly proportional to the square root of the capacity.

As to the maximum current in the arc portion of the ordinary discharge (in which the the current wave consists of one oscillatory and one aperiodic component), an upper limit to its value may be obtained by calculation from the constants of the magneto circuits and the primary current at the moment of "break"*. By such calculations it can be verified that in no case does the maximum current in the inductance portion of the spark given by a high tension magneto of the usual type exceed a few hundred milliamperes†. It is therefore quite certain that when a condenser of considerable capacity is connected with the spark electrodes, the maximum current in the discharge is much greater than that in the discharge which occurs when the condenser is replaced by one of very small capacity, or when the condenser is absent. The great superiority of the igniting action of the ordinary discharge over that of the condenser spark between spherical electrodes cannot therefore be traced to any direct electrical action determined by the value of the current.

In the opinion of the present writer the thermal theory is the only theory which is capable of accounting for the known facts of spark ignition, and it is hoped that the evidence produced in the present communication will tend to renew confidence in it.

Glasgow.
October, 1928.

* The equations required in the calculation are given in the author's 'Theory of the Induction Coil,' Appendix II. pp. 209, 210.

† See also Morgan, 'Electric Spark Ignition,' p. 21, where it is shown that the current in the arc portion is smaller than that in the capacity portion of a magneto spark.

CVIII. *The Phosphorescence of Fused Quartz.*

By A. C. BAILEY and J. W. WOODROW*.

[Plate XXIII.]

DRUMMOND and Webster⁽¹⁾ have shown that a photographic plate will be fogged if kept in contact with certain pieces of quartz which have been previously exposed to ultra-violet light, and they concluded that this effect was most probably due to a phosphorescence of the particular fused quartz which they used. They found that this material would continue to emit a radiation of sufficient intensity to affect a photographic plate for at least three weeks after irradiation with the ultra-violet light. They also found that the effect was enhanced if the quartz plate was kept warm while it was in contact with the photographic plate.

When the above report appeared we were making similar tests, the results of which have confirmed the conclusions of Drummond and Webster and which have also given further information on this type of phosphorescence. Many experiments were carried out upon pieces of fused quartz broken from a large piece which had been obtained from the Thermal Syndicate Co., Ltd., under the trade name of "Vitreosil." It was found that an irradiation of an hour at a distance of 10 cm. from a Cooper-Hewitt quartz mercury arc was sufficient to activate the quartz to such an extent that it would produce a distinct image on a photographic plate in twenty-four hours. The plates were placed in carefully-tested light-proof boxes so as to avoid all possibility of extraneous light-effects. In some of the experiments, the photographic plate was slightly sensitized by a short exposure to a red light before being placed in contact with the quartz.

In one instance a piece of the quartz which had been irradiated for six hours was taken to the dark room, where several people examined it closely in complete darkness. Each observer, however, reported a complete inability to detect the slightest indication of any radiation of visible light, provided the sample was not heated. But this same piece emitted a radiation of sufficient intensity to produce a strong image on the photographic plate even after transmission through a thin piece of glass; and furthermore the ordinary refraction phenomena at the edges of the glass plate were clearly shown in the developed image. This refraction phenomenon and the high transmission of glass obviously

* Communicated by Professor E. C. C. Baly, F.R.S.

indicated a radiation in or near to the visible region of the spectrum.

It has long been known that heating causes a marked increase in the intensity of emission from an excited phosphorescent body and that with continued heating the phosphore soon releases all the energy which has been stored up during the activating process. The irradiated fused quartz was found to possess this property of an activated phosphore, for its power to affect a photographic plate was destroyed by heating for a few minutes in a bunsen flame; however, it could be activated again by a further exposure to ultra-violet radiation. This procedure could be repeated many times, which is in accordance with the results obtained by E. Becquerel⁽²⁾ with fluorspar and by Lenard and Klatt⁽³⁾ with the phosphores which they investigated.

In Pl. XXIII. (figs. 1 and 2) are shown two typical photographs obtained with two different pieces of fused quartz. It is seen that the effects are very prominent at the edges of the broken quartz and that they are not uniform over the surface. Bright spots somewhat circular in shape were produced by the sample shown in fig. 1, while those due to the piece shown in fig. 2 were distinctly rectangular. Many photographs were made both before and after treatment with heat and various acids, but these same spots always appeared in exactly the same places after the quartz had been activated by ultra-violet light. In other samples only one emission-centre was evident, while in still others none at all were present. This was probably due to the manner in which the plate was built up from smaller pieces. These same pieces of quartz were examined carefully under the microscope and photographs were made by allowing diffused light to pass directly through the quartz while in contact with the photographic plate, but nothing irregular could be observed in the region of the spots.

Prof. E. C. C. Baly⁽⁴⁾ has found that fused quartz which had been exposed for a long time to ultra-violet light developed an amethystine colour and became quite opaque to the short-wave ultra-violet. When it was then heated in a powerful blast flame, it emitted a brilliant green phosphorescence which gradually faded away. The pieces of quartz which we had shown to be capable of producing a developable image were also found to emit a green phosphorescence upon heating. The samples were irradiated by exposure to a quartz mercury arc and then taken to a dark room and heated on an electric plate. As soon as they became hot they began to glow very brightly and continued

to do so for more than thirty minutes. A broken quartz flask which had not been used for six months and which had been kept behind glass doors in the laboratory during that time, upon heating gave the characteristic green glow, which was easily observed in the dark room, although it was quite weak.

Tests with natural quartz crystals showed that they did not emit any radiation which would affect the photographic plate or which was visible to the eye upon heating. One of these natural crystals was heated in an electric furnace to a temperature of $575^{\circ}\text{C}.$, at which temperature a change takes place in the form of the quartz, but no phosphorescence was observed. Another crystal was heated to $1200^{\circ}\text{C}.$, but upon being tested exhibited no phosphorescent activity. A third piece from the same crystal was heated very slowly to $1600^{\circ}\text{C}.$, and after cooling was irradiated in the usual manner. Upon heating, this piece gave the same characteristic green glow as was found with the fused quartz plates.

Several other substances were tested for this phosphorescence. Irradiated pyrex glass emitted a radiation upon heating which was visible in a dark room and which was quite similar to that obtained with fused quartz. It would also produce a developable image on a photographic plate without heating. No trace of any phosphorescent activity could be obtained with gypsum. Calcite glowed very brightly for some time when heated; but after it had ceased to glow it could not be reactivated even by an exposure of several hours to the full radiation from a quartz mercury arc.

Fluorite was found to be extremely active and a very short irradiation was sufficient to cause it to emit a bright bluish-violet light upon heating. The fluorite was so sensitive that all pieces tested gave this characteristic glow with a small amount of heating even though it had not received any previous radiation in the laboratory. E. Becquerel⁽²⁾ has found that fluorspar which has been activated by a long exposure to sunlight emits a bright luminescence of visible light when heated to about 90° . After this effect disappears and the crystal has been allowed to cool, it will again emit a visible radiation when the temperature is raised to 90° . Lenard and Klatt have explained this phenomenon by assuming that the fluorspar emits an ultra-violet radiation, which continues after the visible luminescence ceases, and that this in turn activates the cooled fluorspar so that it will again emit a visible radiation when heated a second time. This probably explains why all the pieces of fluorite which we tested gave the characteristic glow when heated even though we had not exposed them to ultra-violet light.

Summary.

In the experiments described here the following facts have been ascertained :—

1. Many samples of fused quartz possess the properties of a phosphorescent body ; that is, they can be excited by ultra-violet light, they will then emit a visible phosphorescent light of considerable strength upon the application of heat, and they can be completely deactivated by bringing to a red heat in a flame.

2. This phosphorescent activity of fused quartz is not uniform, but there is a wide variation between samples and even within the area of a single small piece.

3. Natural quartz crystals do not possess this property of emitting a phosphorescent radiation, but they can be brought into this condition by heating slowly in an electric furnace to a temperature of 1600°C .

4. Pyrex glass, calcite, and fluorite exhibit a prominent phosphorescent activity, but gypsum does not.

References.

- (1) Drummond and Webster, 'Nature,' cxv. p. 837 (1925).
- (2) E. Becquerel, *Compt. Rend.* cxii. p. 557.
- (3) P. Lenard and V. Klatt, *Ann. der Phys.* xv. pp. 225, 425, 633 (1904).
- (4) E. C. C. Baly, 'Spectroscopy,' ii. p. 101 (1927).

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CIX. *The Motion of Electrons in Pentane.* By J. D. MCGEE, *M.Sc., St. John's College, Demonstrator in Physics, University of Sydney*, and J. C. JAEGER, *B.Sc., Deas-Thompson Research Scholar, University of Sydney**.

IN the *Phil. Mag.* (vol. 1. p. 825, Oct. 1925) Professor V. A. Bailey has given a detailed account of a method for investigating the motion of electrons in gases, which is particularly applicable to those gases in which ions are formed by attachment of electrons to molecules as a stream of electrons moves through the gas.

The same apparatus and method have since then been used to investigate the motion of electrons in pentane (C_5H_{12}). This gas was chosen firstly because we had at our disposal,

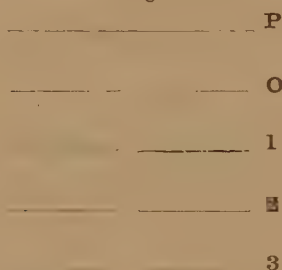
* Communicated by Prof. J. S. Townsend, F.R.S.

through the kindness of Mr. J. G. Burrows of the Chemistry Department, a very pure sample of the liquid, and secondly because Professor E. M. Wellish, in his work on ionic mobilities*, had noticed an "ageing" effect when the gas was allowed to remain in the apparatus for any considerable time. It was therefore of interest to investigate whether these effects still occurred in the more refined apparatus at our disposal, in which the rate of contamination of the gas is very small.

Only a brief account of the theory and experimental procedure is given here; for full details the original paper should be consulted.

2. An electron moving through a gas at a pressure p mm., under the action of an electric force Z volts per cm., will

Fig. 1.



have a drift velocity W in the direction of the electric force, and an agitation velocity U , while the ratio of its kinetic energy to that of a gas molecule is k . Then, if the mean free path of an electron be l , and h be the probability of its attachment to a molecule in collision, the number of electrons remaining free at a plane $z = c$ out of N_0 starting at the plane $z = 0$, the axis of z being the direction of the electric force, will be $N_0 e^{-\alpha c}$, where α is the "coefficient of attachment" which a simple calculation makes $\frac{hU}{lW}$.

The apparatus may be represented diagrammatically as in fig. 1. P, O, 1, 2, 3 are parallel circular plates maintained at such potentials as to produce a uniform field throughout. Electrons are produced by the photoelectric effect of ultra-violet light on a target at P. A narrow stream of electrons and ions passes through the slit in O and diverges, the electrons more than the ions, so that the stream passing

* Phil. Trans. A, ccix. p. 249 (1909).

through the slit in 1 will be richer in ions relative to that passing through the slit in O. This effect is intensified by the continual formation of ions by attachment in the body of the gas. A similar effect occurs at the slit in plate 2, the stream being ultimately collected on plate 3.

Suitable electrical arrangements permit the measurement of the ratios of the current i_1, i_2, i_3 to electrodes 1, 2, and 3. The actual experiment consists in the determination of

$\xi = \frac{i_2}{i_1}$, and $\eta = \frac{i_3}{i_2}$. From these the distribution ratios S_1

and S_2 , of the current passing through the slit to the current arriving at the plane of the slit, can be determined for slits in plates 1 and 2.

Thus

$$S_1 = \frac{\xi(1+\eta)}{1+\xi(1+\eta)}, \quad S_2 = \frac{\eta}{1+\eta}.$$

If, now, n_0 electrons pass the slit in O, $n_0 \epsilon^{-ac}$ will arrive at electrode 1, where c is the interelectrode distance, and

$n_1 = n_0 \epsilon^{-ac} R\left(\frac{Z}{k}\right) = a n_0$ will pass through the slit in 1,

where $R\left(\frac{Z}{k}\right)$ is the distribution ratio at the slit, calculable

from the dimensions of the instrument for given values of Z/k . Similarly, the number of electrons passing through the slit in 2 will be $n_2 = a^2 n_0$. If, in addition, N_0 ions pass through the slit in O, the number passing the slit in 1 will be

$$N_1 = N_0 R(Z) + n_0(1 - \epsilon^{-ac})r = R N_0 + b n_0,$$

where r is the unknown distribution ratio of the ions formed by attachment. Similarly, the number passing through slit 2 is $N_2 = R^2 N_0 + (Rb + ba)n_0$.

But

$$S_1 = \frac{n_1 + N_1}{n_0 + N_0} \quad \text{and} \quad S_2 = \frac{n_2 + N_2}{n_1 + N_1}.$$

Substituting in these and eliminating b , we have

$$a = \frac{S_1(R - S_2)}{R - S_1}.$$

Since R is a known function of Z , a can be derived from the experiments, and we have the relation $R(Z/k) \epsilon^{-ac} = a_1$.

If the force Z and the pressure p be changed to Z/n and p/n respectively, we obtain the additional relation $R(Z/kn) \epsilon^{-ac/n} = a_n$.

From these two equations we obtain

$$\log_{10} a_1 - n \log_{10} a_n = \log_{10} R(Z/k) - n \log_{10} R(Z/kn) \quad (1)$$

and

$$\alpha = \frac{2.3}{c} \{ \log_{10} R(Z/k) - \log_{10} a_1 \} \quad (2)$$

Equation (1) gives k and equation (2) gives α .

3. In practice slight errors are to be expected for the following reasons:—

- (a) Non-uniform distribution of electrons over the upper slit; maximum value computable and negligible.
- (b) Diffusion of the electrons to the sides of the slits.
- (c) Possible asymmetry of the slits.

So calibration is made with hydrogen in which electrons are known always to remain free, and the values of k are well established over a large range of Z/p^* . It is found that, while S_2 plotted against (Z/k) agrees substantially with the theoretical curve, S_1 is consistently lower. This may be ascribed to errors of construction of the apparatus. An

appropriate modification of the theory gives $\alpha = \frac{S_1(R'' - S_2)}{R' - S_1}$,

where R'' and R' are the distribution-ratios for ions obtained from the upper and lower of these curves respectively. The calibration curves used were obtained by Prof. V. A. Bailey and Mr. A. J. Higgs, B.Sc., and were checked before commencing these experiments.

4. The pentane gas was obtained by vaporizing the pure liquid, all precautions being taken to prevent the admixture of foreign gases. After a preliminary drying in preparation, it was dried for twelve months over phosphorus pentoxide at about 250 mm. pressure. The gas was admitted to the apparatus either directly or after a preliminary liquefaction in a small side-tube by liquid air, in which case only the middle third of the liquid was used, the remainder being pumped off. There was no perceptible difference in the results obtained with samples admitted by the different methods.

Samples of gas were tested over several days to examine the possibility of an effect of the ultra-violet light on the gas or an "ageing" effect. Neither was observed, the results remaining constant to within experimental error.

* Townsend and Bailey, Phil. Mag. xlii. (Dec. 1921).

Variations from Boyle's Law were observed with this gas at pressures between 20 and 40 cm., the maximum variation amounting to 4 per cent. Corrections were made for this source of error when reading the pressures in a McLeod gauge.

5. Observations were made at pressures of 8.32, 4.16, 2, and 1 mm., and at forces of 40, 20, 10, and 5 volts per cm., the pressures being originally read as 8, 4, 2, and 1 mm. on the assumption that Boyle's Law held for the gas. But as results were required at values of Z and p increasing in geometrical progression, the determined values of a for given

TABLE I.

Z/p .	p .	Z .	a .	$-\log_{10} a_n$.	Z/k .	y .	k .	a .	$a/p \times 10^3$.
1.25	8.0	10	.476	.322	3.6	.322	2.8	.033	4.1
	4.0	5	.387	.412		.412		.017	
2.5	8.0	20	.520	.284	3.64	.286	5.5	.013	1.6
	4.0	10	.403	.396		.392		.006	
	2.0	5	.303	.519		.524		.003	
5.0	8.0	40	.585	.233	4.70	.237	8.5	.006	0.8
	4.0	20	.452	.345		.342		.003	
	2.0	10	.332	.479		.466		.002	
	1.0	5	.250	.602		.618		.001	
10.0	4.0	40	.433	.358	2.18	.358	18.4	.006	0.8
	2.0	20	.327	.485		.485		.003	
	1.0	10	.234	.631		.633		.001	
20.0	2.0	40	.296	.529	.97	.529	41.2	.014	1.7
	1.0	20	.212	.674		.674		.006	
40.0	1.0	40					77.0		

values of Z were plotted against p , and the values of a at $p = 8.0$ and 4.0 mm. were read off from the curves. The changes in each case were very small. Table I. gives the results of the observations, each number being the mean of several determinations. The values of a at 8.0 and 4.0 mm. are those corrected as above.

To obtain the value of Z/k from equation (1) a series of curves were drawn with

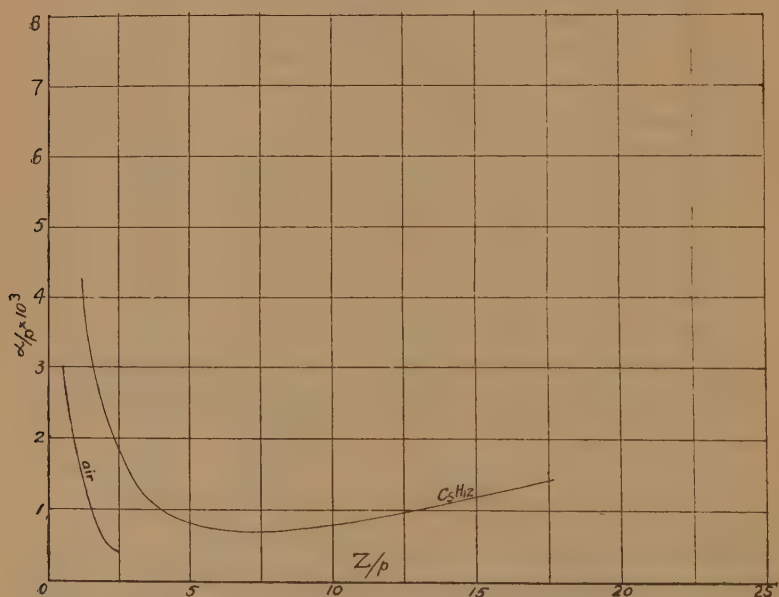
$$x = Z/k \quad \text{and} \quad y = \log_{10} R(Z/k) - n \log_{10} R(Z/kn)$$

for $n = 1, 2, 4$, and 8 , similar to those in fig. 6 in Professor Bailey's paper *. The values of $-n \log_{10} a_n$ were then set

* Phil. Mag. l. p. 825 (Oct. 1925).

off to the same scale on the edge of a strip of squared paper, and the strip moved parallel to the y -axis till the marked points fell as nearly as possible on the curves. The abscissa then is Z/k , and the values of k so determined are shown in Table I. The actual ordinates of the points of intersection of the curves with the strip are given, divided by n , in the column under y in Table I. These should agree with $-\log_{10} a_n$, and the disagreement will show the magnitude of the experimental error. These values of y are used as smoothed values of $-\log_{10} a_n$ for the calculation of α from

Fig. 2.



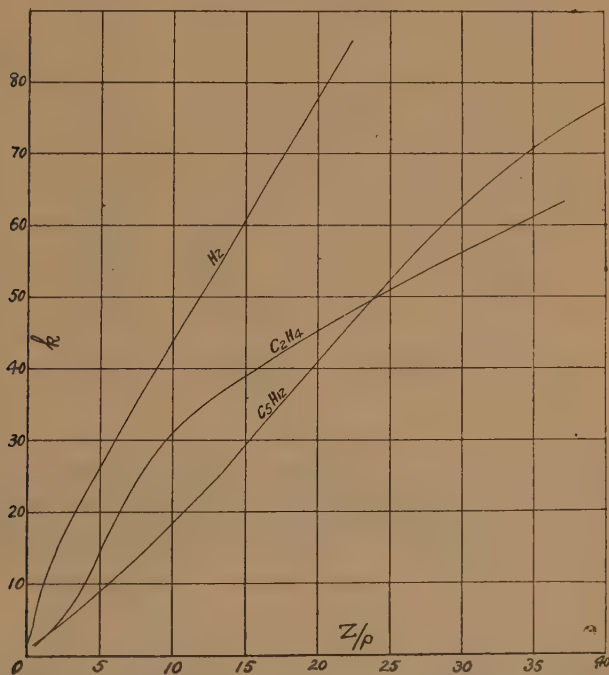
equation (2). The value of k at $Z/p = 40$ is determined directly from the calibration curve, since S_1 and S_2 fall exactly on the theoretical curves at $Z/k = 1$.

6. For the greater part of the range α is very small, being little greater than experimental error, which may be as large as .004. Further at those values of Z/p where α does increase, the results are least reliable, depending on observations at only two pressures. There are definitely very few ions formed, so it is possible that α/p is nearly zero in the perfectly pure gas, the few ions being due to traces of impurity.

The curve showing the variation of α/p with Z/p is given in fig. 2. The curve obtained for air by Professor Bailey is shown also for comparison. They both show the same decrease for increasing Z/p , the values for pentane being consistently higher than those for air.

The curve for k against Z/p is given in fig. 3 with those of ethylene and hydrogen for comparison. The pentane curve is lower than most of the curves, but is not remarkable save for its approximate linearity.

Fig. 3.



7. The values of W were determined in a Townsend diffusion apparatus set up for a research on ethylene by Mr. J. Bannon, B.Sc. We are indebted to him for the value of the eccentricity of the slit, and the constants of the coils producing the magnetic field. The values of W obtained are slightly inaccurate through the presence of a few ions, but the good agreement obtained between experiments at different pressures and forces with the same value of Z/p shows the error to be small. Values of k determined in this instrument agreed well with those obtained in the 3-slit apparatus.

Table II. gives the values of W obtained, each being the mean of several sets of observations at $Z = 40, 20, 10$, and 5 , and $p = 8.32, 4.16, 2.0$, and 1.0 mm.

TABLE II.

Z/p .	p .	Z .	$W \times 10^{-6}$.
60	8.32	5	1.25
1.2	8.32	10	2.39
	4.16	5	2.42
2.4	8.32	20	3.62
	4.16	10	3.68
2.5	2.0	5	3.77
4.8	8.32	40	4.60
	4.16	20	4.62
5.0	2.0	10	4.65
	1.0	5	4.88
9.6	4.16	40	5.10
10.0	2.0	20	5.09
	1.0	10	5.24
20.0	2.0	40	5.50
	1.0	20	5.47
40	1.0	40	6.43

The values of α , and h , of L the mean free path at 1 mm. pressure, and of λ , the fraction of energy lost in a collision, are shown in Table III. These quantities are calculated from the formulæ :

$$U = 1.15 \times 10^7 \sqrt{k}, \quad L = 7 \frac{(WU)}{Z} \times 10^{-16},$$

$$\lambda = 2.46 \frac{W^2}{U^2}, \quad h = 7 \frac{(\alpha W^2)}{Z} \times 10^{-16}.$$

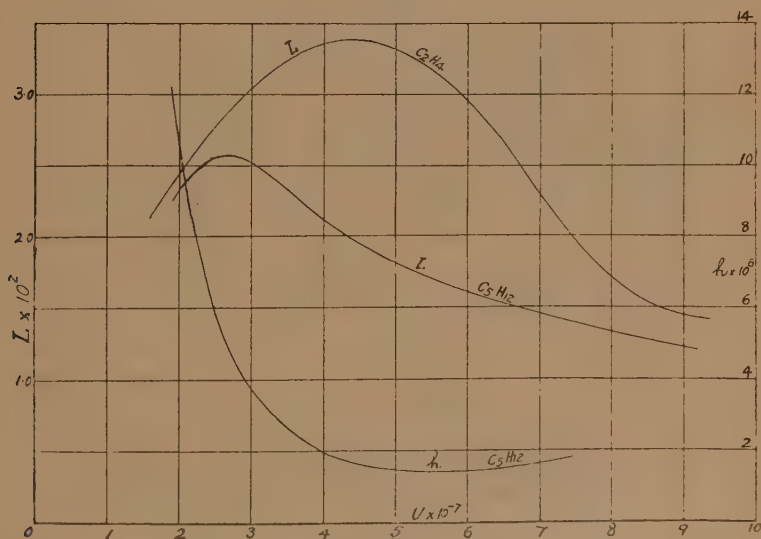
TABLE III.

Z/p .	$W \times 10^{-6}$ cm./sec.	k .	$U \times 10^7$ cm./sec.	$L \times 10^2$ cm.	$\lambda \times 10^2$.	$h \times 10^6$.
625	1.25	1.7	1.5	2.1	1.7	—
1.25	2.42	2.8	1.93	2.26	3.9	13.5
2.5	3.70	4.5	2.46	2.55	5.6	6.1
5.0	4.70	8.8	3.51	2.32	4.4	2.5
10.0	5.10	18.4	4.95	1.77	2.6	1.5
20.0	5.45	41.4	7.4	1.42	1.3	1.8
40.0	6.38	77	10.1	1.13	1.0	—

Fig. 4 gives the curves for L against U for C_5H_{12} and C_2H_4 , and of h against U for C_5H_{12} ; the latter shows a very marked increase of h with decrease of U , beginning in the region of $U = 3 \times 10^7$ cm./sec. The $L - U$ curve for pentane shows a maximum in the early portion of the curve, but there is no minimum in the range used such as occurs with C_2H_4 .

The curve of W against Z/p for pentane is given in fig. 5, with those of C_2H_4 , CO_2 , and H_2 for comparison. It is marked by a very rapid initial rise, the values in the early part of the range being as high as any yet measured,

Fig. 4.



terminated by an almost horizontal portion at the higher values of Z/p .

The curve of λ against U is given in fig. 6, with those of C_2H_4 , CO_2 , and N_2 for comparison. It is noteworthy that the maxima in the L and λ curves occur for the same value of U , indicating that the electrons which penetrate most deeply into the molecules lose the greatest fraction of their energy on collision.

A considerable similarity will be noticed in all the curves between the two hydrocarbons, pentane and ethylene. The curves of $\lambda - U$ show that the gases C_5H_{12} , C_2H_4 , and CO_2 are exceptional in possessing a rapid initial rise and maximum

Fig. 5.

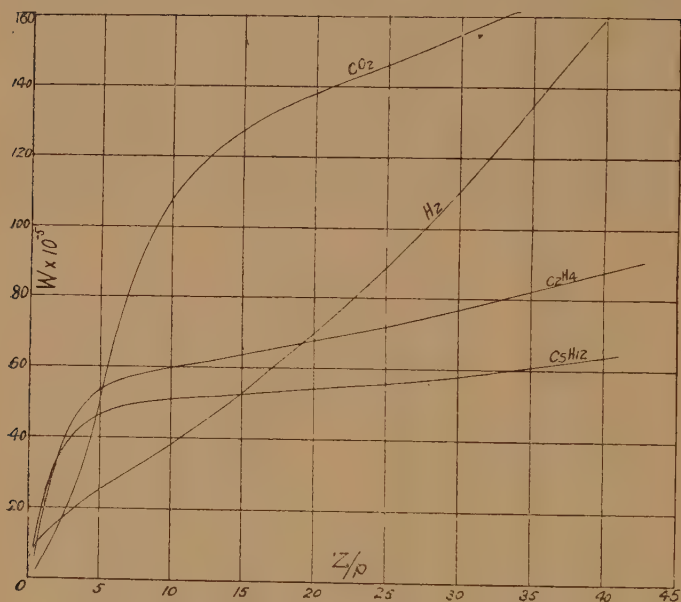
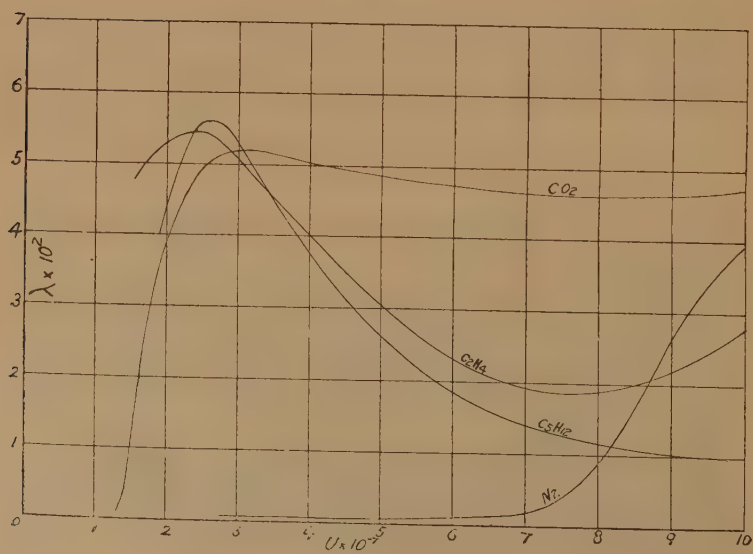


Fig. 6.



in these curves ; all other gases give either consistently low values of λ or a behaviour similar to that of N_2 shown. The large initial values of λ are due to the low initial values of k and high initial values of W . It may be noted that for pentane the maximum in the $\lambda-U$ curve coincides with the rapid rise of the $h-U$ curve, suggesting that this peculiarity may be in some way connected with the formation of ions.

Finally, we wish to thank Professor Bailey, who directed this research, for his advice and assistance during the progress of the work.

CX. *On Spheroidal Harmonics as Hypergeometric Functions.*
By D. M. WRINCH, M.A., D.Sc.*

IN the course of a discussion of harmonics, symmetric about an axis, applicable to surfaces of revolution of some generality, an alternative method was found of constructing harmonics applicable to spheroids, both prolate and oblate.

In the transformation

$$z + i\rho = W(w) = a(e^{iw} + \lambda e^{-iw}) \quad \lambda^2 < 1, \quad (1)$$

where $w = u + iv$, and z and ρ are the usual cylindrical polar coordinates :

$$\left. \begin{aligned} z &= a \cos u (1 + \lambda e^{2v}) e^{-v}, \\ \rho &= a \sin u (1 - \lambda e^{2v}) e^{-v}; \end{aligned} \right\} \quad \dots \dots (2)$$

so that the zero v -level represents the spheroid

$$z, \rho = a[\cos u(1 + \lambda), \sin u(1 - \lambda)],$$

oblate when λ is negative, and prolate when λ is positive, with semi-axes $a(1 + \lambda)$, $a(1 - \lambda)$, $a(1 - \lambda)$, and the level $v = -\infty$ the sphere at infinity.

If the usual form of Laplace's equation for harmonics symmetric about the axis of z be used, namely

$$\left[\rho \frac{\partial}{\partial u} \rho \frac{\partial}{\partial u} V + \rho \frac{\partial}{\partial v} \rho \frac{\partial}{\partial v} \right] V = 0,$$

and if $\cos u = \mu$, and $e^v = \zeta$, the equation for V may be written in the form

$$DV = \lambda D_1 V, \quad \dots \dots (3)$$

* Communicated by the Author.

where, if

$$\mathfrak{S}_\zeta \equiv \zeta \frac{d}{d\zeta},$$

$$D = \frac{d}{d\mu} (1 - \mu^2) \frac{d}{d\mu} + \mathfrak{S}_\zeta (\mathfrak{S}_\zeta - 1), \quad . \quad . \quad . \quad (4)$$

$$D_1 = \zeta^2 \left\{ \frac{d}{d\mu} (1 - \mu^2) \frac{d}{d\mu} + \mathfrak{S}_\zeta (\mathfrak{S}_\zeta + 1) \right\} . \quad . \quad . \quad (5)$$

Under the proviso that $\lambda^2 < 1$, a solution for V may be taken in the form

$$V = f_0 + \lambda f_1 \dots + \lambda^n f_n, \quad . \quad . \quad . \quad (6)$$

where

$$\left. \begin{aligned} Df_0 &= 0, \\ Df_{n+1} &= D_1 f_n. \end{aligned} \right\} . \quad . \quad . \quad . \quad (7)$$

In the case of the sphere when $\lambda=0$, V reduces to f_0 alone, and satisfies the equation $DV=0$. The Legendre function $P_k(\mu)$ satisfies the equation

$$\left[\frac{d}{d\mu} (1 - \mu^2) \frac{d}{d\mu} + m(m+1) \right] P_m(\mu) = 0, \quad . \quad . \quad (8)$$

and ζ^σ the equation

$$[\mathfrak{S}_\zeta (\mathfrak{S}_\zeta - 1) - \sigma(\sigma - 1)] \zeta^\sigma = 0; \quad . \quad . \quad . \quad (9)$$

and therefore, in the usual manner, a harmonic evanescent on the sphere at infinity is given by

$$V = P_k(\mu) \zeta^{k+1} \quad k=0, 1, 2 \dots n, \quad . \quad . \quad (10)$$

which yields the usual form

$$V = P_k(\mu) \binom{a}{r}^{k+1},$$

since $r=a/\zeta$.

If the spherical harmonics be used as a basis, a simple form of harmonic applicable to spheroids can at once be constructed in the form (6).

Thus with

$$f_0 = P_k(\mu) \zeta^{k+1},$$

the equation for f_1 becomes

$$\begin{aligned} Df_1 &= D_1 P_k(\mu) \zeta^{k+1} \\ &= 2(k+1) P_k(\mu) \zeta^{k+3}. \end{aligned}$$

The complementary function for f_1 and, indeed, for f_n is

$$\sum_p d_p P_p(\mu) \zeta^{p+1},$$

To find a particular integral for f_1 , we remark the fact that

$$\begin{aligned} D\zeta^\sigma P_m(\mu) &= \zeta^\sigma P_m(\mu)[-m(m+1) + \sigma(\sigma-1)] \\ &= (\sigma+m)(\sigma-m-1)\zeta^\sigma P_m(\mu). \end{aligned}$$

Thus a particular integral is available in the form

$$f_1 = \frac{2(k+1)}{2(2h+3)} \zeta^{k+3} P_k(\mu).$$

Indeed, suppose that f_n is of the form

$$\sum \alpha_{\sigma, m} \zeta^\sigma P_m(\mu),$$

then

$$\begin{aligned} D_1 f_n &= \zeta^2 \left[\frac{d}{d\mu} (1-\mu^2) \frac{d}{d\mu} + \mathfrak{S}_\zeta (\mathfrak{S}_\zeta + 1) \right] \sum \alpha_{\sigma, m} \zeta^\sigma P_m(\mu) \\ &= \sum \alpha_{\sigma, m} (\sigma-m)(\sigma+m+1) \zeta^{\sigma+2} P_m(\mu), \end{aligned}$$

and therefore a particular integral is available for f_{n+1} in the form

$$f_{n+1} = \sum \alpha_{\sigma, m} \frac{(\sigma-m)(\sigma+m+1)}{(\sigma-m+1)(\sigma+m+2)} \zeta^{\sigma+2} P_m(\mu).$$

The structure of the solutions of the equation is now clear. Suppose we take

$$\begin{aligned} f_0 &= P_k(\mu) \zeta^{k+1}, \\ f_1 &= \frac{1(2k+2)}{2(2k+3)} P_k(\mu) \zeta^{k+3}, \\ f_2 &= \frac{3(2k+4)}{4(2h+5)} \cdot \frac{1(2h+2)}{2(2h+3)} P_k(\mu) \zeta^{k+5}, \end{aligned}$$

and in general

$$\begin{aligned} f_n &= \frac{1 \cdot 3 \dots (2n-1)}{2 \cdot 4 \dots 2n} \cdot \frac{(2k+2)(2h+4) \dots (2k+2n)}{(2h+3)(2h+5) \dots (2h+2n+1)} \\ &\quad \times P_k(\mu) \zeta^{k+2n+1}; \end{aligned}$$

and therefore a solution of the equation is given by

$$\begin{aligned} V &= \zeta^{k+1} P_k(\mu) \left[1 + \frac{1(k+1)}{1!(2h+3)} \lambda \zeta^2 \right. \\ &\quad \left. + \frac{1 \cdot 3(k+1)(k+2)}{2!(2k+3)(2h+5)} \lambda^2 \zeta^4 \dots \right] \\ &= \zeta^{k+1} P_k(\mu) F(k+1, \tfrac{1}{2}; k+\tfrac{3}{2}; \lambda \zeta^2), \end{aligned}$$

where $F(p, q; r; x)$ is the hypergeometric function defined by

$$F(p, q; r; x) = 1 + \frac{pq}{r \cdot 1!} x + \frac{p(p+1)q(q+1)}{r(r+1) 2!} x^2 + \dots$$

This solution is available, as we require, for ζ between unity and zero, since the hypergeometric function $F(a, b; c; x)$ is convergent for $x^2 < 1$.

Thus a typical solution for the sphere

$$V = \zeta^{k+1} P_k(\mu)$$

is corrected for the present case into

$$V = \phi_k(\zeta) P_k(\mu),$$

where

$$\phi_k(\zeta) = \zeta^{k+1} F(k+1, \frac{1}{2}; k+\frac{3}{2}; \lambda\zeta^2),$$

and a solution involving ∞ arbitrary constants

$$V = \Sigma A_k \zeta^{k+1} P_k(\mu)$$

is now developed into

$$V = \Sigma A_k \phi_k(\zeta) P_k(\mu). \dots \dots (11)$$

It is interesting to have the solutions in this form, for it is evidently a simple matter when dealing with applications to write down as many terms as the degree of approximation required makes necessary. The results are therefore readily accessible for practical purposes.

Now the case at present under consideration when

$$\left. \begin{aligned} z &= a \cos u (1 + \lambda \zeta^2) / \zeta = \frac{1}{2} c \cos u (1 / \zeta \lambda^{1/2} + \zeta \lambda^{1/2}), \\ \rho &= a \sin u (1 - \lambda \zeta^2) / \zeta = \frac{1}{2} c \sin u (1 / \zeta \lambda^{1/2} - \zeta \lambda^{1/2}), \end{aligned} \right\} (12)$$

with $c = 2a\lambda^{1/2}$,

is, for λ positive, the well-known and much-discussed case of the prolate spheroid already mentioned, for which, putting

$$z = c \cos u \cosh \xi, \quad \rho = c \sin u \sinh \xi, \dots (13)$$

the form of solution is given by

$$V = \Sigma B_k Q_k(\cosh \xi) P_k(\cos u). \dots \dots (14)$$

This suggests at once that our hypergeometric function $\phi_k(\zeta)$ is a multiple, simply, of the function $Q_k(\cosh \xi)$, where, in view of (12, 13),

$$e^{-\zeta} = \zeta \lambda^{1/2},$$

and we easily find that there is an interesting relation between hypergeometrics whose arguments x and y are connected by the relation

$$y = 4x/(1+x)^2,$$

namely

$$\begin{aligned} x^{\frac{k+1}{2}} F(k+1, \tfrac{1}{2}; k+\tfrac{3}{2}; x) \\ = (y/4)^{\frac{k+1}{2}} F(\tfrac{1}{2}k+\tfrac{1}{2}, \tfrac{1}{2}k+1; k+\tfrac{3}{2}; y). \end{aligned} \quad (15)$$

If we write

$$x = \lambda \zeta^2,$$

and therefore

$$y = 1/\cosh^2 \xi,$$

this becomes, in terms of ξ ,

$$\begin{aligned} e^{-(k+1)\xi} F(k+1, \tfrac{1}{2}; k+\tfrac{3}{2}; e^{-2\xi}) \\ = (2 \cosh \xi)^{-(k+1)} F(\tfrac{1}{2}k+\tfrac{1}{2}, \tfrac{1}{2}k+1; k+\tfrac{3}{2}; 1/\cosh^2 \xi), \end{aligned}$$

which, since

$$\begin{aligned} Q_k(z) = \frac{\Gamma(\tfrac{1}{2}) \Gamma(k+1)}{\Gamma(k+\tfrac{3}{2})} \cdot (2z)^{-k-1} \\ F(\tfrac{1}{2}k+\tfrac{1}{2}, \tfrac{1}{2}k+1; k+\tfrac{3}{2}; 1/z^2) \quad (z^2 > 1), \end{aligned}$$

yields the result :

$$(\xi \sqrt{\lambda})^{k+1} F(k+1, \tfrac{1}{2}; k+\tfrac{3}{2}; \lambda \zeta^2) = \frac{\Gamma(k+\tfrac{3}{2})}{\Gamma(\tfrac{1}{2}) \Gamma(k+1)} Q_k(\cosh \xi),$$

so that our harmonics (11) are, of course, equivalent to the harmonics (14) conventionally taken. Thus our procedure for building up solutions of Laplace's equation in this case yields, in fact, functions which are multiples of the Q_k functions: they have the advantage over the Q_k functions, however, that they more readily lend themselves to practical applications.

In the same manner, if λ be negative, we have

$$\left. \begin{aligned} z &= a \cos u (1 + \lambda \zeta^2) / \zeta = \tfrac{1}{2} d \cos u (1 / \zeta \sqrt{-\lambda} - \zeta \sqrt{-\lambda}), \\ \rho &= a \sin u (1 - \lambda \zeta^2) / \zeta = \tfrac{1}{2} d \sin u (1 / \zeta \sqrt{-\lambda} + \zeta \sqrt{-\lambda}), \end{aligned} \right\}$$

with $d = 2a \sqrt{-\lambda}$,

$$\dots (16)$$

and the unit ζ -level is the oblate spheroid usually taken as $\xi=1$ in the transformation

$$z = d \cos u \sinh \xi, \quad \rho = d \sin u \cosh \xi;$$

so that the relation between ξ and ζ is simply

$$e^{-\zeta} = \zeta \sqrt{-\lambda}.$$

Thus, if in (15) we write

$$x = \lambda \zeta^2 = -e^{-2\zeta},$$

then

$$y = -1/\sinh^2 \xi,$$

and from (15) we deduce that

$$\begin{aligned} V &= \Sigma \alpha_k \phi_k(\zeta) P_k(\cos u) \\ &= \Sigma \beta_k P_k(\cos u) (2 \sinh \xi)^{k+1} \\ &\quad \times F\left(\frac{1}{2}k + \frac{1}{2}, \frac{1}{2}k + 1; k + \frac{2}{3}; -1/\sinh^2 \xi\right) \\ &= \Sigma B_k P_k(\cos u) q_k(\sinh \xi), \end{aligned}$$

which is the usual solution. But we may again point out that our new hypergeometric form of solution (11) allows very simple approximations to be arrived at in all the usual applications concerning oblate spheroids.

It is, in fact, a serious demerit of the treatment of problems relating to spheroids by means of Q_k and q_k functions that these functions do not lend themselves to approximation and computation.

We may also point out that the treatment by hypergeometric functions covers both the cases of prolate and oblate spheroids without the necessity for the separate discussion of the two cases which is called for when the Q_k and q_k functions are used.

Finally, we may direct attention to the fact that the two types of coordinates introduced in (13, 16), as conventionally used in spheroidal problems, are not convenient coordinates to use if a comprehensive view of the problems is taken. We then aim at solving Laplace's equation in the form in which it is applicable to the surface of revolution given by

$$\left. \begin{aligned} z &= a \cos u(1 + \lambda) + \lambda_2 \cos 2u \dots + \lambda_n \cos nu \dots, \\ \rho &= a \sin u(1 - \lambda) - \lambda_2 \sin 2u \dots - \lambda_n \sin nu \dots, \end{aligned} \right\}. \quad (17)$$

and, by developing the treatment which we have just elaborated, we are able, by a simple procedure, to construct harmonics suitable for any more general case. Indeed it appears that there is no essential difference between developing or correcting spherical harmonics so that they may apply to the spheroids, and developing them in a more general manner so that they may apply to any of the surfaces given by the equation (17).

CXI. *The Deterioration of Quartz Mercury Vapour Lamps and the Luminescence of Transparent Fused Quartz.* By A. E. GILLAM and R. A. MORTON*.

[Plate XXIV.]

IN many photochemical reactions in which mercury vapour lamps and fused quartz vessels are used, the efficiency of the processes appears to fall off with time. This may be due to the setting up of chemical equilibria, to a decrease in the output of light from the lamp, or to the development of some degree of opacity in the quartz vessels. There can be no doubt of the fact that most, if not all, makes of quartz mercury lamps deteriorate rather seriously after running for a relatively small number of hours. It is equally certain that fused quartz commonly undergoes a change under the action of light, and that this change is accompanied by some loss in transmission. Little trustworthy information is available as to the extent of these phenomena and as to the connexion which may or may not subsist between them. It is conceivable that the deterioration of the lamps is due to a change in the properties of fused quartz. The purpose of the present investigation is to study the two phenomena a little more closely.

As a result of extended photochemical researches in Prof. Baly's laboratories, a large number of old lamps of the U type have accumulated, and inspection of these shows that the following are the visible signs of ageing :—

(1) The interior surface becomes coated with a brownish black deposit, which is especially noticeable at the thick constriction. In many old lamps the discoloration is distributed over the whole U tube, and the deposit cannot fail materially to reduce the intensity of the transmitted light.

(2) In some lamps the thick quartz at the constriction appears to have been fractured internally, and globules of mercury are seen to be embedded at least a millimetre below the surface. In one case a white mass was seen to be embedded in the quartz.

A number of worn out lamps were broken up and the mercury removed as completely as possible. The black deposit proved to be strongly adherent and resisted the action of strong acids. Boiling aqua regia exerted no

* Communicated by Prof. E. C. C. Baly, C.B.E., F.R.S.

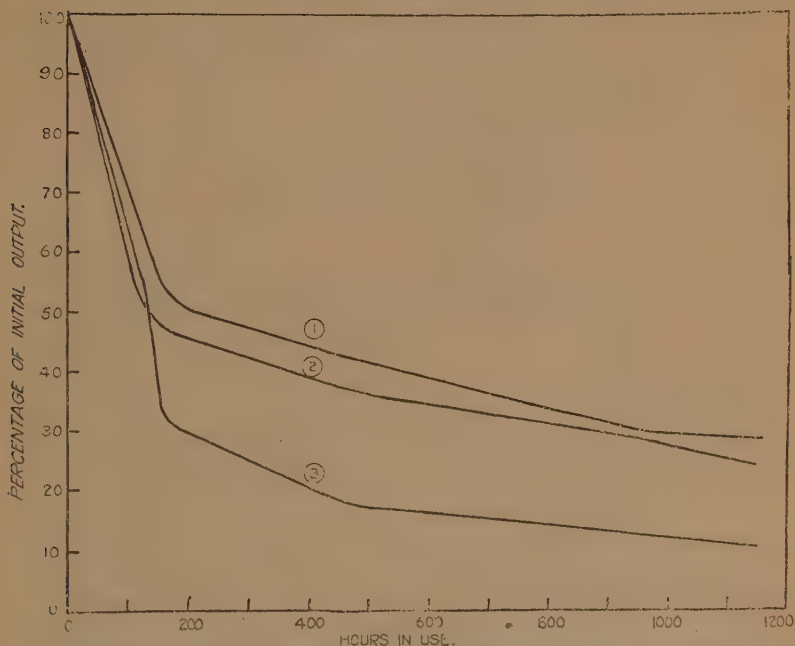
effect, and even after the quartz had been left in contact with aqua regia for some months the stain appeared to be unaffected. If, however, a badly discoloured fragment of quartz was strongly heated in a blow-pipe flame, the black stain was gradually replaced by a white deposit, which again resisted the action of reagents.

No emission of light was seen (*vide infra*) during the heating process. From this it would appear that the deposit is unlikely to consist of mercury or mercury compounds, but may possibly consist of elementary silicon. It has been suggested (Drane, Brit. J. Actinotherapy, June, 1926) that in certain evacuated lamps having a tungsten or molybdenum anode, thin layers of compounds of these metals become deposited on the inner surface of the arc tubes and act as selective filters. Drane also states that "a decrease in intensity is observed as the lamp is used, due essentially to partial devitrification of the silica glass of the arc tube." Prolonged heating causes the "amorphous fused silica to change over to tridymite and cristobalite in varying amounts, depending upon the conditions of heating and the presence of catalysts, if any. In this respect the hot mercury vapour is not without influence upon the devitrification which occurs upon the inner surface of the arc tube." Drane's remarks occur in a paper on "The operation of quartz mercury vapour lamps," and are only incidental to his main theme. The detailed evidence for these views and particularly for the part played by devitrification in the deterioration process does not appear to have been published as yet.

It may be of interest briefly to summarize the evidence for deterioration. The formation of ozone in the surrounding air is much more noticeable with a new lamp than with an old lamp. From this it can be inferred (*cf.* Lenard, *Ann. Physik*, 1900, i. p. 486) that the emission of very short wave ultra-violet rays decreases with time. Spectrum photographs taken with Schumannized plates show not only that the emission from an old lamp is materially less than that from a new lamp for all wave-lengths, but that the spectrum does not extend quite so far into the ultra violet. Actinometric records of the output at different stages in the history of a lamp exhibit the deterioration very clearly, and it is interesting to note that although a gradual decrease in emission is shown over the whole ultra-violet spectrum, a selective decrease is manifest in the very short wave ultra violet. The falling off is most noticeable on the short wave side of $250\text{ }\mu\mu$.

In the figure the life-history of an atmospheric burner as given by three different chemical methods of gauging ultra-violet intensity is shown (for details of these methods see Gillam and Morton, *Journ. Soc. Chem. Ind.* 1927, xlv. p. 417). It will be seen that the very high initial output is maintained only for a small fraction of the effective life of the lamp, but that the decrease in intensity tends afterwards to occur much more slowly. The nitrate actinometer (*ibid.* p. 415) registers the greatest drop in output, a fact of some

Fig. 1.



Decrease in output of a 230-volt atmospheric mercury vapour lamp with time. The curves represent the output as measured by :

1. Anderson and Robinson's method.
2. The acetone-methylene-blue gauge.
3. The nitrate method.

significance, since the chemical change which is measured occurs almost exclusively with rays shorter than $270\mu\mu$. The spectroscopic and actinometric data we have obtained are perhaps a little unexpected. There are clearly two factors in the deterioration process, a shortening of the spectrum in the extreme ultra-violet and a gradual loss in

transmission of a less selective type. The relative importance of these two factors changes considerably during the life of the lamp. In the early stages the quartz remains relatively free from dark stains or deposits, but the output decreases very rapidly and the deterioration is largely confined to the extreme ultra-violet. As the period of operation lengthens the short wave limit of transmission ceases to move in the direction of longer wave-lengths. The output does not, however, remain steady, but decreases uniformly over the spectrum, just as if an increasingly dense "grey" screen were being interposed between the incandescent vapour and the arrangement for measuring the light intensity.

In order to test whether the drop in output was due to the formation of a metastable variety of quartz less transparent than the ordinary variety, the atmospheric burner was emptied and the mercury removed as completely as possible. The lamp had been in use for nearly 200 hours. The whole of the lamp was carefully cleaned with nitric acid, washed thoroughly, and heated to redness. The mercury was then replaced and the output of the lamp again measured. No appreciable improvement occurred as a result of such treatment, showing that the deterioration is independent of the luminescence phenomena which will be discussed later.

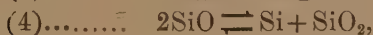
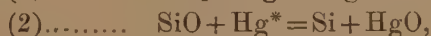
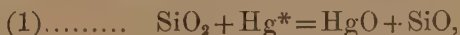
Several hypotheses may be formulated to account for these results. It is possible that light emission from the mercury permanently affects the quartz in some way. Baly ('Spectroscopy,' vol. ii. p. 332) writes as follows :

"It is well known that fused silica in layers about 2 mm. thick is markedly transparent to ultra-violet light to as far as wave-length 1900 Å. If this material is exposed to the radiation from a quartz mercury lamp for some days, then, providing it is kept cool, the silica develops an amethyst colour exactly similar to that of natural amethyst quartz. Not only has the silica now developed a visible colour, but it has also become opaque to ultra-violet light of short wave-length. This new condition of the silica is metastable, and if it is heated to about 500° C., or if it is crushed, it emits a brilliant green phosphorescence, and returns to its normal colourless state which is transparent to short wave ultra-violet light."

Our observations confirm the above quotation, but we are satisfied that the phenomenon has little or no connexion with the problem of the deterioration as observed with the 230-volt lamps available to us. The running temperature is so

high that the new state would, as we shall show, prove quite unstable. A closer investigation of the effect of light on fused quartz has shown that when a piece of the amethystine material is heated a thermo-luminescence occurs, and the quartz tends to revert to its original condition. Even more significant is the fact that the absorption spectra of irradiated and unirradiated fused quartz differ but little, and that in any case the difference could only account for a very small fraction of the observed deterioration.

A second hypothesis may be formulated as follows: In the luminous mercury vapour a large number of excited atoms must exist, and collisions with the walls of the lamp may sometimes be inelastic and the reactions



might all occur.

If this view were correct one might expect to find in an old lamp, silicon, silicon monoxide, and possibly silica formed in the cycle of changes and deposited on the vitreous quartz surface.

Silicon monoxide (see Mellor's 'Comprehensive Treatise on Inorganic Chemistry,' vol. vi. p. 235) is a dark amorphous solid prepared by the interaction of silica and carbon in the electric furnace. It burns in oxygen, decomposes water with evolution of hydrogen, and is soluble in warm alkaline solutions. It may now be asked whether the dark stain found on the inside of old mercury vapour lamps does in fact consist of silicon monoxide. It will be seen that the properties of the deposit (see above) are different from those of the monoxide, but are in agreement with those of silicon. Whilst there is therefore no evidence of the accumulation of solid silicon monoxide, it is scarcely possible to account for the observations without assuming its existence in the vapour state while the lamp is in operation.

Bonhoeffer (*Z. Physik. Chem.*, 1928, cxxxi. p. 363) has studied the absorption spectrum of silicon monoxide vapour, and has recorded bands at 241.4, 234.4, 234.2, 229.9, 225.6, and 221.5 $\mu\mu$. These observations are of great interest because they provide an explanation of the marked decrease in the output of ultra-violet rays in the short wave region of the spectrum. If the ideas we have suggested are true,

the dominating factor in the early stages of the deterioration will be the absorption of rays up to $242\ \mu\mu$ by silicon monoxide vapour. On switching off the current some dissociation may occur, and the only possibilities are the deposition on the inside walls of a fresh layer of silica, of silicon, or of silicon monoxide in the solid state. Every time the lamp is used some silicon monoxide vapour must again be formed by the interaction of silica and activated mercury, and it is reasonable to expect that the solid deposit, whatever it may be, will gradually grow more dense. Minute specks of a fresh layer of silica or silicon will hinder the transmission of the vitreous quartz, and no doubt the concentration of silicon monoxide vapour in the discharge will approach constancy.

The two factors in the deterioration thus appear successively, and the actinometric data are in complete agreement with this mechanism.

An acceptable hypothesis should account for the fact that the brown deposit first appears at the constriction on the negative arm of the lamp tube. Since activated mercury atoms have a very short life period of the order 10^{-8} sec., the probability of collisions between activated atoms and silica is much greater in a more restricted space. Indeed, it may be stated that the deposit does in fact tend to occur preferentially wherever the shape of the tube causes the bombardment to be unusually severe. It will thus be seen that the observed facts are again consistent with the mechanism of deterioration which has been put forward.

Unfortunately no very ready means of overcoming the ageing effect emerges from the discussion.

Although the phosphorescence of fused quartz now appears to have little connexion with the behaviour of mercury lamps, it is well worthy of study on its own account. Our experiments had been in progress for some time before we became aware of those of Bailey and Woodrow detailed in the preceding communication. On account of the very similar trend of the results obtained in Prof. Woodrow's laboratory and in the present work, it was thought advisable to publish simultaneously.

A *résumé* of our experiments may now be given. In the first place it was found that the effect of ultra-violet rays on fused silica varied with different specimens. Some turned out to be excellent "phosphors," whilst others were apparently quite ineffective. One sample gave a faint but unmistakable green phosphorescence immediately after the lamp was turned out, and in a dark room this light could

be seen for several minutes. Emission of light persists for a very long time, since images can be recorded on a photographic plate (exposure 12–48 hours, see Pl. XXIV.) at least a fortnight after activation. No difference is detectable between the images obtained with the quartz in contact with the emulsion, and the quartz separated from the photographic plate by a slip of glass. The emission which affects the plate must therefore consist largely of rays longer than $325\text{ }\mu\mu$. Samples which had ceased to phosphoresce visibly became luminous again on heating. This thermo-luminescence has been observed to occur in two stages. Gentle heat produces light of a yellow-green colour, whilst with stronger heating the emission is bright blue-green. When a piece of activated quartz is heated with a fine blowpipe the yellow emission is seen to travel outwards from the point at which the flame impinges on the solid, and as the quartz becomes hotter a second zone of bluish light is seen to follow. The two phenomena are quite distinct, and the zones may be a couple of centimetres apart.

The light emission appears to correspond with (a) a highly unstable state, the return to the normal being accompanied by spontaneous emission of visible light; (b) a less stable state, the reversion from which to the normal is accompanied by a slow spontaneous emission, which may not terminate for months, and is detected photographically; (c) a metastable state, in which the absorbed energy can be retained practically indefinitely provided the quartz be not heated much above room temperature. The three stages are thus, a phosphorescence of short duration, another of longer persistence, and a third thermo-luminescence effect.

It is possible that (b) is merely a continuation at a low light intensity of the process which occurs in (a). The fact that two separate zones were observed in the "thermo-luminescence" may mean that the entire sequence of luminescence can be obtained with freshly activated quartz on application of heat, the yellow light being due to the first fall in energy level (which normally occurs spontaneously) and the bluish light being due to the reversion to the normal state from the metastable state associated with the pink colour. These doubtful points might be cleared up if a spectrographic record of the wavelengths emitted could be obtained. Unfortunately the intensity is too low for this purpose. In studying the relation between thermo-luminescence and temperature we have noticed no well defined discontinuity. A sample non-luminous at room temperature became feebly luminous

when dropped into water at as low a temperature as 55°C ., but in order to effect complete deactivation it is necessary to heat at least as high as 400°C .

It is interesting to record that specimens of fused quartz from test tubes sent from the United States to Professor E. C. C. Baly by Mr. W. T. Anderson, Jun., showed no sign whatever of phosphorescence or of thermo-luminescence. Natural rock quartz also appears to be completely unaffected by ultra-violet rays. There is no detectable difference in density between the specimens of fused quartz which show the phenomena and those which do not. Neither can we detect any change in density after irradiation.

A small piece of optically true fused quartz (thickness 0.1 in.) was obtained, and after prolonged irradiation under cold water was found to be activated in the sense that light was emitted freely on heating. Investigation of the absorption spectrum of this sample (which was very faintly amethystine), showed that no loss in transparency was detectable for ultra-violet rays longer than 220μ . Considerable difficulty was experienced in determining whether activation resulted in the development of opacity in the region $200\text{--}220\mu$. Some experiments showed a distinct difference between the transmissions of the active and deactivated materials in this region, but the effect was on so small a scale that absolute certainty of its reality is still to be sought. In order to settle this point it seems necessary either to enhance the whole activation phenomenon or to increase the delicacy of the spectroscopic test. We find that fused quartz test tubes do not develop sufficient opacity to affect appreciably the reading with any of the well known chemical methods of measuring ultra-violet intensity. The activation of the quartz has, however, been found by Baly to result in a reduction of yield in photosyntheses requiring rays shorter than 220μ .

If the activation process is concerned with metastable varieties of silica one might expect to find some evidence of incipient devitrification. Microscopic examination and experiments on polarization disclosed not the slightest trace of such an effect. This agrees with the density determinations since the values for various samples of fused quartz fell within the limits 2.210 and 2.228, whilst those of the rock quartz were 2.667 and 2.676. Since, however, the density of cristobalite is 2.21, the measurements of density do not exclude devitrification.

The above results seem to indicate that the phosphorescence and thermo-luminescence of fused silica is due to

the presence of a minute trace of impurity. Such an explanation is perfectly in accord with general notions on luminescence and is indeed supported by the uneven structure of the images illustrated.

Preliminary attempts to prepare silica phosphors using oxides of heavy metals in small amounts, with sodium fluoride as a flux, have not so far proved successful. Such phosphors possess considerable interest because the transparency of the fused quartz medium or diluent should, in favourable cases, allow the absorption spectra of the phosphors to be photographed.

The observations of Chapman and Davies ('Nature,' 1924, cxiii. 309) and Ludlam and West (*ibid.* 389) and also of Curtis (*ibid.* 495) show that quartz discharge tubes exhibit an intense phosphorescence after the current has been switched off. In all cases, it would now seem as if the mechanism of activation is the absorption of radiant energy of very short wave-lengths (90–220 $\mu\mu$). The phosphorescence obtained by using the light from a quartz mercury lamp as the source of activating rays is very much feebler than that obtained with discharge tubes in which ultra-violet rays in the Lyman region are freely generated. Nevertheless, the slow activation which we have studied seems to be essentially the same process, especially since the thermo-luminescence always appears, irrespective of the mode of activation. Ludlam and West favoured the view that the phosphorescence of transparent fused silica was due to minute traces of impurity, a conclusion strongly supported by our own observations.

Summary.

1. There are two factors operating in the deterioration of quartz mercury lamps, (*a*) a shortening of the spectrum confined to the extreme ultra violet, and (*b*) a non-selective loss in transmission.

2. The first factor preponderates for the first 150–200 hours and shows itself as a rapid fall in output. After this period the effect becomes fairly constant. During the subsequent history of the lamp the second factor plays an increasingly important part, but manifests itself much more slowly.

3. It is suggested that the first effect may possibly be due to the formation of silicon monoxide vapour inside the lamp, and the second effect may arise from the gradual deposition of a film of opaque elementary silicon.

4. The luminescent properties of fused quartz after treatment with ultra-violet rays have been studied. Little or no connexion subsists between these properties and the deterioration of quartz mercury lamps.

5. Three types of luminescence phenomena have been observed with transparent fused quartz :

- (a) a brief visible phosphorescence ;
- (b) a phosphorescence of long duration ;
- (c) a thermo-luminescence.

6. The balance of evidence points to the view that traces of impurity must be present in those samples of fused silica which exhibit luminescence.

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CXII. *The Electrification of Air by Friction.* By AGNES W. McDIARMID, M.A., *George A. Clark Scholar of the University of Glasgow* *.

ALTHOUGH a number of investigations have recently been described in which the charge of electricity produced by the friction of solid bodies on one another was measured, it appears to be doubtful whether electricity can be produced by the friction of gases on solids. Lenard † stated that when a drop of water splashes against a metal plate a positive charge goes to the water and a negative charge to the surrounding air, and Kelvin ‡ that air bubbled through water is negatively electrified. More recently experiments have been made with the direct object of testing the question whether electricity is produced between solids and gases. E. Perucca § found that mercury vapour flowing along a solid body produced electrification, while M. A. Schirmann || stated that mercury vapour, when flowing at great velocity in a glass tube, produced sparks at the places of greatest friction. It is, however, not quite certain that the electricity developed in these experiments was not due to

* Communicated by Prof. E. Taylor Jones.

† *Wied. Ann.* xlvi. p. 584 (1892).

‡ *Proc. Roy. Soc.* xlvii. p. 335 (1894).

§ *Zeits. f. Physik*, xxxiv. 2-3, pp. 120-130 (1925).

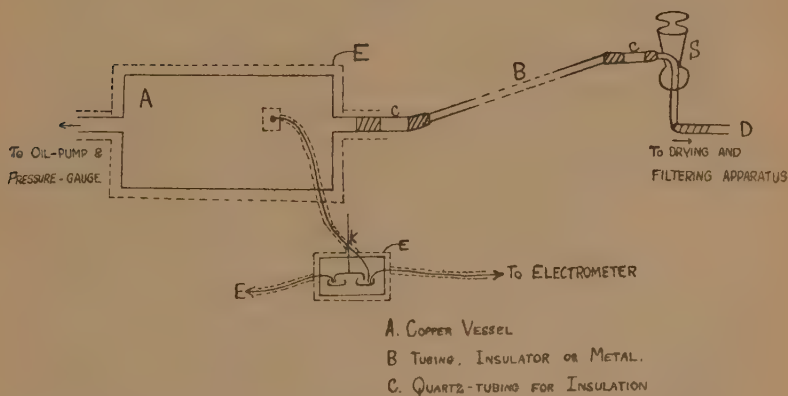
|| *Zeits. f. Physik*, xlvi. 3-4, pp. 209-236 (1927).

minute drops of liquid or to particles of dust contained in the air.

There seems to be definite evidence that dust clouds become electrified when in motion, in which case the electricity is probably due to the impact of solid particles on one another. Also, it has been shown that the number of volts developed by blowing a given mass of dust into a cloud increases very rapidly as the size of the dust particles decreases*.

It seems, therefore, not unlikely that a similar effect might, in suitable conditions, be produced by the impact of gas particles on a solid surface. The experiments described below were undertaken with the object of discovering

Fig. 1.



whether or not electrification can result from the friction of dry, dust-free air with solid surfaces. It was thought that such an investigation might lead to the discovery of facts which would be of use in the formation of a theory concerning the nature of frictional electricity in general.

Apparatus.

The simplest method of bringing about friction between air and solid bodies appeared to be to make a current of air pass quickly through tubes of the various solids. Fig. 1 is a diagram of the apparatus used. It consists essentially of a narrow tube B, and a copper vessel A. The whole

* G. B. Deodhar, Proc. Phys. Soc. xxxix. part 3 (1927); and W. A. Douglas Rudge, M.A., Proc. Roy. Soc. (1914).

apparatus could be rendered air-tight by shutting stop-cock S, and evacuated by means of an oil-pump, a pressure-gauge registering the pressure to which it was evacuated. Tube B was insulated from A and from the stop-cock S by means of short but adequate lengths of quartz tubing. The copper vessel, of volume about 5000 c.c., was connected by thin copper wire to one pair of quadrants of a Dolezalek electrometer. The other quadrants were permanently earthed. The vessel stood on a slab of paraffin-wax and was protected from external influences by means of an earthed metal shield surrounding it. The wire from vessel A led to a mercury key, K, insulated in paraffin-wax, through which connexion could be made either with the earth or with the electrometer. The mercury key and the connecting wire to the electrometer were surrounded by earthed metal shields, the key being worked by a long insulated handle protruding through the shield.

It was necessary that the air used to produce the friction should be dry and perfectly free from dust. With this in view, in the first form of the experiment S was joined to an earthed metal tube 12 in. \times 1½ in., containing tightly-packed glass-wool, which in turn was joined to a U-tube containing calcium chloride. Several readings were taken with this form of drying and filtering apparatus, but it was felt that there was no proof that the smaller dust particles were being removed. Aitken*, in his paper "On the Number of Dust Particles in the Atmosphere," describes experiments in which he investigated the filtering powers of different lengths of tightly-packed cotton-wool. By means of cloud experiments he concluded that filtration is perfect with 4 in. of tightly-packed wool, provided that the air is allowed to pass through very slowly. In the final form of the present experiment the air to be used for producing friction with the tubes was first passed very slowly through concentrated sulphuric acid and then through a glass tube 1½ in. in diameter, containing 8 in. of very tightly-packed glass-wool that had been soaked in concentrated sulphuric acid. From this the air passed through a stop-cock S' into a very large carboy, air-tight and connected to D, in fig. 1, then through an earthed metal tube, 1 in. in diameter, containing less tightly packed glass-wool.

Stop-cock S' was shut and the whole apparatus, *i. e.*, carboy and copper vessel, evacuated to a few millimetres pressure by means of an oil-pump. S' was then opened in

* Trans. Roy. Soc. Edin. vol. xxxv. p. 1 (1890).

such a way that air entered extremely slowly into the apparatus, after having passed through the sulphuric acid and the glass-wool. This procedure was repeated several times. Stop-cocks S and S' were then shut. This method of storing dried, filtered air was adopted so as to allow the passage of air very quickly through tube B. It could only be passed through quickly if filtered beforehand.

The essential difference from the earlier type of drying and filtering apparatus lies in the extremely slow passage of the air through the concentrated sulphuric acid and the tightly-packed glass-wool.

The readings obtained with both types of apparatus were of the same order of magnitude. Various suspensions were tried for the electrometer needle, that finally used being a silk fibre coated with platinum, and this proved extremely sensitive. With 12 volts on the needle the deflexion of a spot of light thrown on a scale 90 cm. distant was 600 mm./volt. The scale was calibrated by the difference of potential due to a known current passing through a known resistance. The only drawback to this suspension was that, after a large deflexion, the needle took a few minutes to return to the original zero-point. The electrometer was used throughout at sensitivity varying from 300 to 600 mm./volt. The insulation of the apparatus was tested frequently.

The friction tubes (B) used were of various materials, the insulators being glass, quartz, ebonite, and the metals iron, aluminium, copper, brass, lead. They were of various lengths and diameters and were dried before insertion.

The apparatus, up to stop-cock S, was rendered air-tight by shutting S, and was then exhausted to any required pressure by means of the oil-pump. During this procedure the vessel A was earthed. The position of the spot of light on the scale was noted. The vessel and one pair of quadrants of the electrometer were then insulated by lifting out key K. S was opened quickly, S' being kept shut, and dried, filtered air from the carboy rushed through B into vessel A. The deflexion of the spot on the scale and the time of inrush of the air were noted.

In another form of the experiment the vessel A was kept earthed, and tube B, if of metal (or a tinfoil covering wound tightly round B, if B was of insulating material), was connected with the insulated quadrants, the tube B being in every case surrounded by an earthed shield. The tube B was earthed while the apparatus was being exhausted, then B was insulated, air allowed to run through, and the deflexion noted.

The main idea of the experiment was thus to allow dry, dust-free air to pass rapidly through tubes of various materials, and hence into a metal vessel, either the vessel or the tube being connected to one pair of quadrants of the electrometer. The insulation of the apparatus was very satisfactory, and when the vessel was unearthed by raising key K, no deflexion of the needle was observed until air rushed through tube B. The capacity of the apparatus was determined approximately, and from the capacity and the potential corresponding to any deflexion of the needle the charge on the vessel A or the tube B could be obtained.

Results.

At first no attempt was made to obtain quantitative results, the primary objective being to discover whether the air and the tubes did actually become charged by the friction between them, owing to the air running through the tubes.

In every case, both with metals and insulators, a measurable deflexion of the electrometer needle was noted, showing that the passage of air into vessel A through tube B changed the potential of vessel A.

The potential to which vessel A was raised was of the order of magnitude of 1 volt, the charge given to it being of the order of $\frac{2}{3}$ e.s.u.

It was also found invariably that the deflexion obtained when vessel A was connected to the electrometer was opposite in sign to that obtained when tube B was connected to the electrometer. That is, the charge on vessel A, after the inrush of air, was opposite in sign to that on tube B.

Insulators

In each case, when a tube of insulating material was used, it was found that a second rubbing produced only a small deflexion, but that if the tubes were allowed to rest for a day or so, or in the case of glass or quartz were heated strongly, sometimes while still inserted in the apparatus, and then allowed time to cool between rubs, the deflexion of the electrometer needle was approximately the same as at the first rub. This was the case both when the vessel was connected and when the tube was connected to the electrometer. Thus, for example, a quartz tube 1 cm. \times 61 cm. gave on one occasion, on successive rubbings, deflexions +90, +15, +12, +10, whereas, after heating the tube strongly and rubbing it one hour later, the deflexion was +102. Again, a glass tube, 7 mm. \times 79 cm., gave on successive rubbings -600, -55, -20 mm. deflexion. Another glass tube 6 mm. \times 79 cm.

gave, when the rate of inrush of the air was very small, a deflexion -30 mm. At the second rubbing the speed was greatly increased and the deflexion was -75 mm. A third rubbing at this increased speed gave -10 mm.

These facts seem to point to the existence of a maximum charge for each tube, independent of the amount of air that passes through it.

Various experiments also pointed to the fact that the charge developed depends directly on the length of tube B, other things being equal. Thus, a tube 7 mm. \times 79 cm. gave on one occasion a deflexion -246 mm. This tube was allowed to rest and 46.5 cm. of it were cut off and rubbed under the same conditions as before. This time the deflexion was -154 mm., so that the charge developed on the air was directly proportional to the length of the tube. Many experiments confirmed this.

Occasionally reversals in the sign of electrification were noted. The general conclusion was, however, that the charge on the glass and ebonite used was positive, and on the quartz negative. The vessel A, and hence the air, was charged oppositely to the tube in each case.

A very large number of experiments were made, especially with glass tubes of various bores and lengths, and with various velocities of flow of the air. The difficulty of obtaining exact quantitative results, *e. g.*, as to effect of varying velocity of flow, of difference of bore, of varying length of tube, lies mainly in that of keeping the state of the surface rubbed exactly the same in different experiments. The changes in the state of the surfaces due to exposure to the atmosphere, and also to the friction, make exact results on such points difficult to obtain. These changes in the state of the surfaces may also account for the occasional reversals in the sign of electrification. Owing to the difficulty of keeping the surfaces in a definite state the quantitative results varied considerably on different occasions, but provided the rubbing tubes were examined after given treatment the results were always of the same order of magnitude.

A series of experiments with glass tubes, all of length 78 cm. and of bore varying from $\frac{1}{2}$ mm. to 1.5 cm., seemed to point to the fact that the electrification increases with the speed of flow. Some of the results are given in the following table:—

Bore in mm.	0.5	2	4	5	7	10
Time of flow in secs. ...	300	28	8	7	6	5 $\frac{1}{4}$
Deflexion in mm.	5	90	150	505	845	950

The above series would seem to point to a limiting case in which no tube is present and the air rushes directly into vessel A without previous passage through any narrow tube. To investigate this a cylindrical brass vessel, A, was used in the same position as A in fig. 1. The same precautions about insulation, etc., were taken. A hole 2 cm. in diameter was cut in one end of the vessel, and this was filled up with a plug of paraffin-wax, as thin as possible, but able to stand the strain when A was exhausted to a pressure of a few millimetres. A length of steel rod, 25 cm., was sharply pointed, and to its blunt end was attached a length of ebonite tubing with a cross-piece of ebonite to act as an insulating handle. The metal part was earthed, and precautions were taken to prevent charging of A by induction when a hand holding the sharp rod was brought near A. The procedure was to exhaust A, keeping it earthed, and then to push the steel point into and through the plug of wax. This held the vacuum. A was then unearthed and insulated. The spot of light on the scale remained steady, showing that the insulation was satisfactory. The steel rod was then pulled out and air rushed through the orifice thus made into the vessel. The spot of light remained steady, showing that no charge was produced by the inrush of air through the orifice. The size of the opening was varied so that the time of inrush of the air varied from 7 seconds to 14 seconds. In no case was any deflexion of the electrometer needle produced. It seems, then, that the presence of a tube was necessary to produce the electrification, and that the fact that wider tubes gave a bigger charge was due to the fact that they also permitted a greater velocity of flow.

This point was then tested directly with several tubes. For a glass tube 7 mm. \times 79 cm., when the time of flow of air was 7 secs., the deflexion was -246 , while when the time of flow was 45 secs. the deflexion was -10 , and when it was 9 secs. it was -130 . These results are typical and point to the fact that electrification of the air increases with its velocity of flow through the tubes.

Metals.

The metals used were iron, copper, brass, and aluminium, and were of the ordinary commercial grade of purity. With these, reversals in the sign of electrification were more frequent than with the insulators. The general conclusion was, however, that the charge on the brass and copper was positive, and on the iron and aluminium negative, the air being oppositely charged in each case. The results obtained

as to the effect of varying the speed of flow and the length of the tube were the same as in the case of insulators.

General Conclusions.

The results detailed above established at least the fact that the passage of a rapid current of air through a tube causes the current to carry with it charged particles of air and leaves the tube oppositely charged. According to the kinetic theory of gases the collision frequency of particles of the gas with one another and with the walls of the tube is increased by a negligible amount by the flow of the gas. It would thus appear probable that the quick flow of the current of air through the tube into the metal vessel is not primarily the source of the charged particles of air but serves mainly to remove from the vessel particles of air that have been charged by impact, due to their molecular motion, with the walls of the tube.

In May of this year J. Tagger* published a paper describing experiments wherein he measured the potential to which a horizontal helix of chrome-nickel wire, from which the surface layer of gas had been removed, was raised, whilst near its melting-point, by the impact of the molecules in the mass of air surrounding it. With high temperatures, *i. e.*, temperatures near the melting-point, a potential of 30 volts was reached.

There remains to explain the fact that the charge increased with increase in velocity of the air through the tubes. Three possibilities suggest themselves:—

- (1) The inrush of the air through the tube gives to the molecules a slightly larger velocity component in the direction of the flow. As the impacts of the molecules with the tube are in all directions, the charges produced in air at rest may balance one another. The additional velocity component in a fixed direction, though small, caused by the motion of the air through the tube, may call into being charges which will not be balanced by any other charges.
- (2) Quick motion of the air through the tube may be necessary to prevent the charges on the air and on the tube from re-combining and so masking the effect.

* *Phys. Zeits.* xxix. pp. 304-308, May 15 (1928).

- (3) Slow motion of the air through the tube may enable the tube to adsorb a layer of air so that only a very small part of the air passing through the tube is in actual contact with the material of the tube, or at least with a material different from itself. Only the air which passes through first will be in such contact, the remainder coming into contact only with a film of air.

Tagger's experiments, in which no restraint whatever was put on the direction of impact of the particles of air and the wire, seem to nullify the first alternative, although the two experiments differ so much as to make comparison difficult.

In conclusion, the writer wishes to express her thanks to Professor Taylor Jones for his continued advice and encouragement and for many helpful suggestions. The experimental work was performed in the Research Laboratories of the Natural Philosophy Department of the University of Glasgow.

October 1928.

CXIII. *Development of Formulæ for the Constants of the Equivalent Electrical Circuit of a Quartz Resonator in Terms of the Elastic and Piezo-Electric Constants.* By P. VIGOUREUX, M.Sc., of the National Physical Laboratory*.

CONSIDER a parallelepiped of alpha or low temperature quartz cut with its edges parallel respectively to the optic axis o , the electric axis e , and that axis which is perpendicular to o and to e , and which we shall call the third axis, t , and let o , e , and t denote the lengths of the edges of the parallelepiped.

If the potential difference between the two faces perpendicular to e be V , and the stress along e be $\frac{F}{ot}$, in the direction tending to produce extension, the extension y of the axis e , and the charge Q liberated at either of the $o.t$ faces, are given by the formulæ:

$$y = K_0 F - HV, \dots \dots \dots (1)$$

$$Q = K_1 V + HF, \dots \dots \dots (2)$$

* Communicated, by permission of the Radio Research Board, by Sir J. E. Petavel, K.B.E., F.R.S.

where o, t, e, y are in centimetres, Q and V in electrostatic c.g.s. units, and F in dynes; H is the piezo-electric constant, of value approximately 6.4×10^{-8} ; K_1 is the capacity between the two $o.t$ faces, namely,

$$K_1 = \frac{t \cdot o}{4\pi e} \cdot P, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where P , the permittivity, is approximately 4.55; the value of K_0 is readily calculated from the equation

$$\text{stress} = E \cdot \text{strain},$$

and found to be

$$K_0 = \frac{e}{t \cdot o} \frac{1}{E} \cdot . \quad . \quad . \quad . \quad . \quad (4)$$

The dimensions of H in electrostatic units are $L_1 M^{-\frac{1}{2}} T P^{\frac{1}{2}}$. The coefficient K_0 is not a capacity; formula (1) shows that its dimensions are $M^{-1} T^2$.

The modulus of elasticity E is generally taken as 7.85×10^{11} dynes per cm.^2 along e and t ; it has a higher value along the axis o .

The signs of the terms HV and HF in equations (1) and (2) depend upon the direction of the applied electric field and the orientation of the parallelepiped with respect to certain angles and edges of the complete quartz crystal out of which it is cut, but in any pair of equations such as (1) and (2) the signs are always opposite.

If there be, as before, a difference of potential V between the two $o.t$ faces, and if the stress along the third axis t be $\frac{F}{oe}$, the extension y_t of the axis t , and the charge Q liberated at either $o.t$ face, are given by the formulæ:

$$y_t = K_0 F + \frac{t}{e} H V, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$Q = K_1 V - \frac{t}{e} H F; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

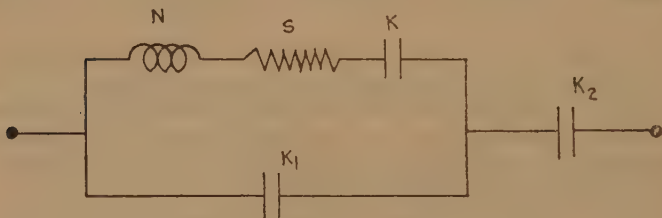
the value of K_1 is, of course, the same as before, but the value of K_0 is now

$$K_0 = \frac{t}{oe} \frac{1}{E} \cdot . \quad . \quad . \quad . \quad . \quad (7)$$

If no stress be exerted by mechanical means, and if the potential difference applied between the $o.t$ faces be alternating, the forced extension produced will also alternate, but will be so small that it could only be detected by using a

very high voltage between the two *o.t* faces; if, however, the frequency of the applied difference of potential happens to coincide with one of the natural frequencies of the parallelepiped, the amplitude of vibration is greatly increased, because of resonance, and can be detected in several ways. In particular, the difference of potential may be applied by means of two metal plates of dimensions *o.t* placed close to the *o.t* faces of the piece of quartz and connected to the terminals of the condenser of an oscillatory circuit tuned approximately to one of the natural frequencies of the quartz, the coil of the oscillatory circuit being loosely coupled to the output coil of a valve generator. As the frequency of the generator passes through the natural frequency of the quartz, the quartz vibrates strongly and reacts on the oscillatory circuit, causing a diminution of current in the coil. This reaction was first observed by

Fig. 1.



Cady⁽⁴⁾, and was later studied in considerable detail by D. W. Dye⁽¹⁾, who showed experimentally that the behaviour of the vibrating quartz was nearly identical with that of a circuit shown in fig. 1; the capacity marked K_2 in the figure is that of the air-gap between the electrodes and the quartz, and is independent of the properties of the quartz. It is the object of the present paper to show how the effective inductance N and the effective capacity K can be estimated from the dimensions of the quartz, its modulus of elasticity, and its piezo-electric constant.

This problem is intimately connected with that of longitudinal vibrations. It is convenient first to calculate the simpler case by working out expressions for a thin bar; it will be assumed that the variations which take place in its cross-section during the vibrations are negligible. This condition is not strictly satisfied, but the influence of the effect on the final results is very small indeed.

A bar of length e , supported at its middle point, is

subjected to a periodic stress $\frac{F}{to} = \frac{F_0}{to} \cos wt$, assumed uniformly applied throughout its length. We write here $w = 2\pi n$, where n is the frequency of the applied stress; it is required to calculate the displacement z of any point x at any time t . It is obvious that, since we are concerned with vibrations at or near resonance, the damping is of prime importance in determining the amplitude of the resonant vibrations; if it were neglected the equation of motion would lead to an infinitely large value for z at resonance.

Taking the origin of coordinates at the middle point of the bar, and writing E for the modulus of elasticity, s for the specific gravity, and Q for the damping coefficient, the equation of motion is

$$\frac{\partial^2 z}{\partial t^2} = \frac{E}{s} \frac{\partial^2 z}{\partial x^2} + Q \frac{\partial^3 z}{\partial x^2 \partial t}, \quad \dots \quad (8)$$

which is the form given by H. Lamb⁽²⁾ and applied recently by Cady⁽³⁾ to the particular problem of quartz resonators.

The coefficient Q includes not only the viscosity, which is small, but also the air-damping and the resistance to motion due to the mode of support of the bar and to other causes. The term representing air-damping is usually written as

$$-P \frac{\partial Z}{\partial t},$$

but the particular integral of the above equation being identical with the particular integral of the equation

$$\frac{\partial^2 z}{\partial t^2} + \frac{\pi^2}{e^2} Q \frac{\partial z}{\partial t} = \frac{E}{s} \frac{\partial^2 z}{\partial x^2}, \quad \dots \quad (9)$$

it is permissible to represent the whole of the resistance due to motion by the single term $Q \frac{\partial^3 z}{\partial x^2 \partial t}$. The value of Q is

in all cases very small compared with $\sqrt{\frac{E}{s}} e$, where e is the

length of the bar. Writing α^2 for $\frac{E}{s}$, we have

$$\frac{\partial^2 z}{\partial t^2} = \alpha^2 \frac{\partial^2 z}{\partial x^2} + Q \frac{\partial^3 z}{\partial x^2 \partial t} \quad \dots \quad (10)$$

Two sets of conditions are required for the complete solution, namely the initial conditions which serve to determine the complementary function, and the boundary conditions which are used in the calculation of the particular integral.

The initial conditions give the state of the bar just before the periodic stress is applied ; they are, say,

$$z = f_1(x), \quad \text{and} \quad \frac{\partial z}{\partial t} = f_2(x), \quad . . . \quad (11)$$

where f_1 and f_2 are functions of x . They might even both be zero in our case, but will be considered arbitrary for more generality.

The boundary conditions supply data relating to the state of the bar at one or more particular values of x at any time t . In the present case they are that

$$\text{when} \quad x = 0 \quad z = 0, \quad . . . \quad (12)$$

$$\text{when} \quad x = \frac{1}{2}e \quad \frac{\partial z}{\partial t} = \frac{F_0}{otE} \cos wt, \quad . . . \quad (13)$$

for since the ends of the bar are free, the stress there cannot be influenced by the motion of the bar, but is equal to the applied stress.

Since the force impressed on the bar is of frequency n , part of the motion must take place at this frequency ; the particular integral will be

$$F(x) \cos wt + F_1(x) \sin wt,$$

where the functions $F(x)$ and $F_1(x)$ are determined by the boundary conditions.

The solution satisfying the equation (10) and the boundary conditions (12) and (13) is

$$\begin{aligned} z = & \sum_0^{\infty} A_k e^{-\frac{1}{2} Q \frac{\pi^2}{e^2} (2k+1)^2 t} \sin \frac{\pi}{e} (2k+1)x \\ & \cos \frac{\pi}{e} (2k+1) \sqrt{a^2 - \frac{Q^2 \pi^2 (2k+1)^2}{4e^2}} t \\ & + \sum_0^{\infty} B_k e^{-\frac{1}{2} Q \frac{\pi^2}{e^2} (2k+1)^2 t} \sin \frac{\pi}{e} (2k+1)x \\ & \sin \frac{\pi}{e} (2k+1) \sqrt{a^2 - \frac{Q^2 \pi^2 (2k+1)^2}{4e^2}} t \\ & + F(x) \cos wt + F_1(x) \sin wt, \quad . . . \quad (14) \end{aligned}$$

with the conditions that

$$\left. \begin{aligned} F(0) &= F_1(0) = 0, \\ F(\tfrac{1}{2}e) &= \frac{F_0}{otE}, \\ F_1(\tfrac{1}{2}e) &= 0, \end{aligned} \right\} . . . \quad (15)$$

where the symbol “¹” represents differentiation with regard to x before substitution of $\frac{1}{2}e$ for x .

The first part of the solution decreases rapidly with time, and after a very short interval the particular integral alone is of importance; moreover, the degree of damping is greater for the overtones than it is for the fundamental, since it is

$$\frac{-\frac{1}{2}Q\frac{\pi^2}{e^2}(2k+1)^2 t}{e},$$

and the transient free motion therefore becomes more and more nearly sinusoidal before vanishing.

Once $F(x)$ and $F_1(x)$ have been determined, the coefficients A_k and B_k can, if desired, be calculated by the method usually employed for the Fourier series.

Making use of (11) and putting $t=0$ in (14), we have

$$f_1(x) = \sum_0^{\infty} A_k \sin \frac{\pi}{e} (2k+1)x + F(x);$$

therefore

$$\begin{aligned} \int_0^{\frac{1}{2}e} f_1(x) \sin \frac{\pi}{e} (2k+1)x dx \\ = \frac{1}{4}e A_k + \int_0^{\frac{1}{2}e} F(x) \sin \frac{\pi}{e} (2k+1)x dx, \end{aligned} \quad (16)$$

from which A_k is calculated.

In the same way, when $t=0$,

$$\begin{aligned} f_2(x) = \frac{\partial z}{\partial t} = \sum_0^{\infty} -\frac{1}{2}Q \frac{\pi^2}{e^2} (2k+1)^2 A_k \sin \frac{\pi}{e} (2k+1)x \\ + \sum_0^{\infty} \frac{\pi}{e} (2k+1) \sqrt{\alpha^2 - \frac{Q^2 \pi^2 (2k+1)^2}{4e^2}} B_k \sin \frac{\pi}{e} (2k+1)x \\ + w F_1(x), \end{aligned}$$

and proceeding as before, we find

$$\begin{aligned} \int_0^{\frac{1}{2}e} f_2(x) \sin \frac{\pi}{e} (2k+1)x dx \\ = -\frac{1}{4}e A_k \frac{1}{2}Q \frac{\pi^2}{e^2} (2k+1)^2 \\ + \frac{1}{4}e B_k \frac{\pi}{e} (2k+1) \sqrt{\alpha^2 - \frac{Q^2 \pi^2 (2k+1)^2}{4e^2}} \\ + w \int_0^{\frac{1}{2}e} F_1(x) \sin \frac{\pi}{e} (2k+1)x dx. \quad \dots \quad (17) \end{aligned}$$

The values of A_k and B_k are thus given by equations (16) and (17), and can be evaluated when the functions f_1, f_2, F , and F_1 are known.

In the present case we are not concerned with the values of A_k and B_k , but only with the steady motion, and need only find F and F_1 .

The particular integral is

$$z = F(x) \cos wt + F_1(x) \sin wt, \quad \dots \quad (18)$$

where $F(x)$ and $F_1(x)$ must satisfy the general equation and the conditions (15), namely

$$F(0) = F_1(0) = 0,$$

$$F'(\tfrac{1}{2}e) = \frac{F_0}{otE},$$

$$F_1'(\tfrac{1}{2}e) = 0.$$

The procedure is to substitute for z and its derivatives in equation (10), and to equate the sine and cosine terms, thus obtaining two simultaneous differential equations in F and F_1 from which F and F_1 are determined by a linear differential equation of the fourth order. This equation is

$$[(A^4 + w^2 Q^2)D^4 + 2a^2 w^2 D^2 + w^4]F = 0, \quad \dots \quad (19)$$

and the same for F_1 .

The expression for F , deduced from the above equation, thus contains four arbitrary constants, as also does the expression for F_1 , but the eight constants are related by four equations, which are easily obtained by substituting the values of F and F_1 in either of the original simultaneous differential equations in F and F_1 .

It therefore remains to determine only four constants from the four boundary conditions (15), when the following final result is obtained :

$$\left. \begin{aligned} F &= 2A \cos vx \sinh ux + 2B \sin vx \cosh ux, \\ F_1 &= 2B \cos vx \sinh ux - 2A \sin vx \cosh ux, \end{aligned} \right\} \quad \dots \quad (20)$$

where

$$\left. \begin{aligned} 2A &= \frac{F_0}{otE} \frac{u \cos \tfrac{1}{2}ev \cosh \tfrac{1}{2}eu - v \sin \tfrac{1}{2}ev \sinh \tfrac{1}{2}eu}{(u^2 + v^2) (\cos^2 \tfrac{1}{2}ev \cosh^2 \tfrac{1}{2}eu + \sin^2 \tfrac{1}{2}ev \sinh^2 \tfrac{1}{2}eu)} \\ \text{and} \\ 2B &= \frac{F_0}{otE} \frac{u \sin \tfrac{1}{2}ev \sinh \tfrac{1}{2}eu + v \cos \tfrac{1}{2}ev \cosh \tfrac{1}{2}eu}{(u^2 + v^2) (\cos^2 \tfrac{1}{2}ev \cosh^2 \tfrac{1}{2}eu + \sin^2 \tfrac{1}{2}ev \sinh^2 \tfrac{1}{2}eu)}, \end{aligned} \right\} \quad \dots \quad (21)$$

with

$$\text{and } \left. \begin{aligned} u^2 &= \frac{1}{2} \frac{w^2 (\sqrt{a^4 + w^2 Q^2} - a^2)}{a^4 + w^2 Q^2} \\ v^2 &= \frac{1}{2} \frac{w^2 (\sqrt{a^4 + w^2 Q^2} + a^2)}{a^4 + w^2 Q^2} \end{aligned} \right\} \dots \dots (22)$$

To find the total extension of the rod at any instant we must double z and write $\frac{1}{2}e$ for x . We then obtain, after a very simple reduction,

$$y = 2 \frac{F_0}{otE} \frac{1}{u^2 + v^2} \frac{u \sinh eu + v \sinh ev}{\cos ev + \cosh eu} \cos wt \\ + 2 \frac{F_0}{otE} \frac{1}{u^2 + v^2} \frac{v \sinh eu - u \sinh ev}{\cos ev + \cosh eu}. \quad (23)$$

In the present case the stress $\frac{F_0}{ot}$ is produced by the difference of potential between the $o.t$ faces, according to equations (1) and (2). From equation (1) we see that a difference of potential V_0 tends to produce an extension $-HV_0$ which is equivalent to a force $-\frac{H}{K_0} V_0$.

Equation (1) shows that the restoring force for an extension y is

$$\frac{y + HV}{K_0}.$$

This, being a restoring force, is in the negative direction according to the convention adopted; when it is substituted for F in equation (2), we obtain

$$Q = K_1 V - H \frac{y + HV}{K_0} \\ = \left(K_1 - \frac{H^2}{K_0} \right) V - \frac{H}{K_0} y, \quad \dots \dots (24)$$

an expression for the total quantity of electricity through the resonator at any time.

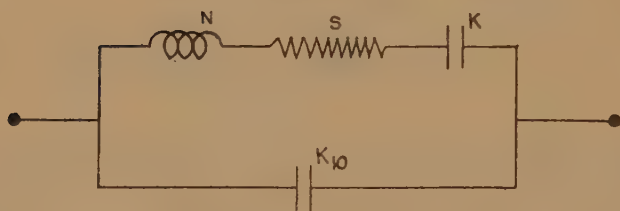
Writing

$$V = V_0 \cos wt \quad \text{and} \quad F_0 = -\frac{H}{K_0} V_0,$$

and substituting the value of y from equation (23), we obtain for the quantity of electricity

$$\begin{aligned} Q = & \left(K_1 - \frac{H^2}{K_0} \right) V_0 \cos wt \\ & + 2 \frac{H^2}{K_0^2} \frac{V_0}{otE} \frac{1}{u^2 + v^2} \frac{u \sinh eu + v \sin ev}{\cos ev + \cosh eu} \cos wt \\ & + 2 \frac{H^2}{K_0^2} \frac{V_0}{otE} \frac{1}{u^2 + v^2} \frac{v \sinh eu - u \sin ev}{\cos ev + \cosh eu} \sin wt. \quad (25) \end{aligned}$$

Fig. 2.



This expression is comparable with that for the quantity of electricity through a circuit represented in fig. 2, where we easily find

$$\begin{aligned} Q = & K_{10} V_0 \cos wt \\ & - \frac{w^2 N - \frac{1}{K}}{\left(w^2 N - \frac{1}{K} \right)^2 + w^2 S^2} V_0 \cos wt \\ & + \frac{wS}{\left(w^2 N - \frac{1}{K} \right)^2 + w^2 S^2} V_0 \sin wt. \quad . \quad . \quad . \quad (26) \end{aligned}$$

In order that the two expressions may be identical, we require

$$K_{10} = K_1 - \frac{H^2}{K_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

$$\frac{U}{U^2 + W^2} = -2 \frac{H^2}{K_0^2} \frac{1}{otE} \frac{1}{u^2 + v^2} \frac{u \sinh eu + v \sin ev}{\cos ev + \cosh eu},$$

$$\frac{W}{U^2 + W^2} = 2 \frac{H^2}{K_0^2} \frac{V_0}{otE} \frac{1}{u^2 + v^2} \frac{v \sinh eu - u \sin ev}{\cos ev + \cosh eu},$$

in which we have written for brevity

$$w^2 N - \frac{1}{K} = U,$$

$$wS = W.$$

It is easily found from the above that

$$U = -\frac{1}{2} \frac{K_0^2}{H^2} \text{otE} \frac{u \sinh eu + v \sin ev}{\cosh eu - \cos ev}, \quad . \quad . \quad (28)$$

$$W = \frac{1}{2} \frac{K_0^2}{H^2} \text{otE} \frac{v \sinh eu - u \sin ev}{\cosh eu - \cos ev}. \quad . \quad . \quad . \quad (29)$$

For all the resonant frequencies of the parallelepiped $w^2 Q^2$ is small compared with α^4 , and we have from equations (22) the approximate relations :

$$v = \frac{w}{\alpha},$$

$$u = \frac{1}{2} \frac{w^2 Q}{\alpha^3},$$

$$\sinh eu = eu = \frac{1}{2} e \frac{w^2 Q}{\alpha^3},$$

$$\cosh eu = 1 + \frac{1}{2} e^2 u^2 = 1 + \frac{1}{2} e^2 \frac{1}{4} \frac{w^4 Q^2}{\alpha^6},$$

$$\sin ev = \sin \frac{ew}{\alpha},$$

$$\cos ev = \cos \frac{ew}{\alpha}.$$

Therefore

$$\begin{aligned} -Nw^2 + \frac{1}{K} = -U &= \frac{1}{2} \frac{K_0^2}{H^2} \text{otE} \frac{\frac{w}{\alpha} \sin \frac{ew}{\alpha}}{1 - \cos \frac{ew}{\alpha}} \\ &= \frac{1}{2} \frac{K_0^2}{H^2} \text{otE} \frac{w}{\alpha} \cot \frac{1}{2} \frac{ew}{\alpha} \\ &= \frac{1}{2} \frac{K_0^2}{H^2} \text{otE} \frac{w}{\alpha} \tan \left\{ \left(k + \frac{1}{2} \right) \pi - \frac{1}{2} \frac{ew}{\alpha} \right\}. \end{aligned}$$

But the condition for the resonance of the circuit of fig. 2 is that U should be approximately zero, so that

$$(k + \frac{1}{2})\pi - \frac{1}{2} \frac{ew}{a} \doteq 0$$

or

$$n \doteq (2k + 1) \frac{a}{2e}, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where n denotes the frequency.

For the fundamental mode of vibration

$$n \doteq \frac{a}{2e}.$$

We have

$$U = Nw^2 - \frac{1}{K} = -\frac{1}{2} \frac{K_0^2}{H^2} \text{otE} \frac{w}{a} \cot \frac{1}{2} e \frac{w}{a}.$$

To obtain the separation of N and K , differentiate this expression thus:

$$\begin{aligned} \frac{dU}{dw} = 2Nw = & -\frac{1}{2} \frac{K_0^2}{H^2} \text{otE} \frac{1}{a} \cot \frac{1}{2} e \frac{w}{a} \\ & + \frac{1}{2} \frac{K^2}{H^2} \text{otE} \frac{w}{a} \frac{1}{2} \frac{e}{a} \text{cosec}^2 \frac{1}{2} e \frac{w}{a}; \end{aligned}$$

and since near resonance

$$\cot \frac{1}{2} e \frac{w}{a} \doteq 0 \quad \text{and} \quad \text{cosec} \frac{1}{2} e \frac{w}{a} \doteq 1,$$

we have

$$\begin{aligned} N & \doteq \frac{1}{4} \frac{K_0^2}{H^2} \text{otE} \frac{1}{2} \frac{e}{a^2} \\ & \doteq \frac{K_0^2 \text{ote}}{H^2 8} s \\ & \doteq \frac{K_0^2 M}{H^2 8}, \quad . \quad . \quad . \quad . \quad . \quad (31) \end{aligned}$$

where s is the density and M the mass of the bar.

Near resonance the value of U is approximately zero, so that

$$NKw^2 \doteq 1.$$

Substituting in this the values of n and N as found by equations (30) and (31), we obtain

$$K \doteq \frac{H^2}{K_0^2} \frac{8}{otes} \frac{4e^2}{4\pi^2(2k+1)^2a^2}$$

$$\doteq \frac{H^2}{K_0^2} \frac{8}{\pi^2} K_0 \frac{1}{(2k+1)^2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (32)$$

by making use of the expression for K_0 , formula (4).

The expression for S can be obtained in the same manner from equation (29) by calculating the value of w , from which it is found that

$$S \doteq \frac{M}{8} \frac{K_0^2}{H^2} \frac{(2k+1)^2}{e^2} \pi^2 Q. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (33)$$

This expression for S is of no direct use, because Q represents several types of resistance to motion, the chief of which are viscosity, air-damping, and the effect of the support of the bar. The resistance S also includes the effect of dielectric loss in the quartz, due to the electric fields produced by the alternating stress. The value of S is determined directly from the reaction of the resonator on an electric circuit by methods developed by W. G. Cady⁽⁴⁾ and D. W. Dye⁽¹⁾. The above analysis therefore leads to the conclusion that the piezo-electric quartz bar, in the neighbourhood of one of its resonant frequencies, has the same impedance as an electrical circuit made up of a resistance S , an inductance N , and a capacity K in series, shunted by a condenser K_{10} , as in fig. 2, where the values of N , S , K , K_{10} are given by formulæ (31), (33), (32), and (27).

The auxiliary quantities M , K , and K_0 are

$$M = ote \cdot s,$$

$$K_1 = P \frac{ot}{4\pi e}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

$$K_0 = \frac{e}{to} \frac{1}{E}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

In the case of a disk cut perpendicular to the electric axis and vibrating along the electric axis, the product ot , wherever it occurs in the formulæ, should be replaced by $\pi o^2 = \pi t^2$, the sectional area.

Similar formulæ hold for vibrations along the third axis t , if instead of H we write $\frac{t}{e} H$, and if we use for K the value

given by formulæ (7), namely $\frac{t}{oe} \frac{1}{E}$. The values of K and K_{10} are therefore the same as before, and N is altered in the

ratio of t^2 to e^2 so that the resonant frequency is altered in the ratio of e to t .

The above values hold only in the neighbourhood of resonance; by this we mean that they hold good for all values of $\frac{ew}{a}$ for which one can write without great error

$$\left| \cot \frac{1}{2} \frac{we}{a} \right| = \left| \left(k + \frac{1}{2} \right) - \frac{1}{2} \frac{ew}{a} \right|.$$

Thus, whenever the value of w is such that

$$\left\{ (2k+1) - \frac{ew}{a} \right\}^2$$

is small compared with unity, the electrical circuit gives a good representation of the quartz resonator.

Since the decrement of quartz is very small, and therefore the range of frequency over which it reacts on an electrical system only a small fraction of the fundamental frequency—at most one in a thousand, and generally not more than one in five thousand,—the above condition is always satisfied for the range of frequency with which we are concerned.

The equivalence between mechanical vibrating systems and electrical oscillatory circuits is, of course, well known, and S. Butterworth⁽⁵⁾ pointed out several years ago that many problems could be simplified by making use of the analogy. W. G. Cady⁽³⁾ subsequently mentioned the equivalence in the particular case of quartz rods, and K. S. Van Dyke⁽⁶⁾ gave expressions similar to the above for N , K , and K_{10} .

The equivalent capacity K can be measured experimentally, for example by D. W. Dye's⁽¹⁾ methods, and the average piezo-electric constant H can be calculated from formula (32). This requires that the quartz should be free from electrical twinning as well as from optical twinning, a condition very rarely met with even in the best specimens. An important figure, which is in some ways a measure of the suitability of the quartz for resonators and oscillators, is the ratio of K_1 to K . From equations (3) and (32) this is found to be for the fundamental:

$$\frac{K_1}{K} = \frac{\pi}{32} \frac{H^2}{E} P,$$

which, with the values of H , E , and P , given at the beginning of this paper, is 140. Most pieces of quartz give a value well above this figure, but the nearer the value is to 140 the better is the quartz, provided its damping S is low.

It is necessary to point out that the overtone frequencies are not given exactly by the formula (30):

$$n = (2k + 1) \frac{a}{2e}, \quad . \quad . \quad . \quad . \quad (30)$$

where k is an integer, because the formula was developed without taking into account the lateral motion of the vibrating bar. For a long thin rod the variations are small, although irregular, as shown by Giebe and Scheibe⁽⁸⁾.

An important result can be deduced from the above analysis, concerning the strain at any point of the vibrating rod. Since in all cases u is small, approximate expressions for 2A and 2B of formula (21), in the neighbourhood of resonance, are

$$2A = \text{constant} \cdot u,$$

$$2B = \text{same constant} \cdot \frac{w}{a}.$$

In an approximate expression we can neglect A in comparison with B, and we obtain

$$Z = F \cos wt + F_1 \sin wt,$$

substituting for F and F_1 by (20) gives

$$Z = \text{constant} (\sin vx \cosh ux \cos wt + \cos vx \sinh ux \sin wt),$$

and since x is never greater than $\frac{1}{2}e$, $\sinh ux$ can be neglected in comparison with unity, and the simple expression for Z is

$$Z = \text{constant} \cdot \sin vx \cdot \cos wt.$$

The displacement is therefore sinusoidal, being zero at the centre and a maximum at the ends, where $x = \pm \frac{1}{2}e$, and the strain is a maximum at the centre and decreases to zero at the ends. This was illustrated in a beautiful manner by Giebe and Scheibe⁽⁸⁾ with their luminous resonators.

This work has been carried out under the auspices of the Radio Research Board, to whom thanks are due for permission to publish.

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CXIV. *The Power Relation of the Intensities of the Lines in the Optical Excitation of Mercury.*—Theory I. By E. GAVIOLA, Ph.D., Fellow of the International Education Board*.

IN a former paper by Wood and Gaviola † we have seen that the prediction of Wood ‡, that the intensity of some of the mercury lines appearing in the fluorescence of the optically-excited vapour (3650 for example) should be proportional to the cube of the exciting intensity, while others, such as 3654, 4358, etc., are proportional to the square, and others (2537) to the primary intensity itself, has been proved experimentally in a large range of variation. It has been found, for instance, that a 10·5-fold increase of the intensity of the exciting light was able to increase the intensity of the fluorescence line 3654 about 120 times, and of the line 3650 no less than 1200 times. The optically-excited vapour represents then a light-source which radiated energy, regarded in the light of the line 3650, apparently increases with the third power of the absorbed energy, or at least with the third power of the exciting intensity. This seems to be in contradiction with the principle of conservation of energy, and one must ask oneself, if it were possible to increase a hundred-fold the intensity of the mercury arc, would 3650 increase a million times in its brightness? And if so, where would the energy come from? To answer those questions it is necessary to make a quantitative study of the relations between the intensities of the primary exciting lines of the arc and of the secondary fluorescence lines in the vapour. We shall see that this theory will enable us at the same time to explain many of the results of Wood's experimental observations that could not be understood otherwise, for instance, the differences in the falling off of the intensity of the diverse lines along the cross-section of the tube when viewed "end on," and the changes in the intensity curves if gases are admitted to it.

The Intensity of 3650.

If we consider the diagram of energy levels of fig. 1 we see that the line 3650 is emitted by the 3^3D_3 level. Its intensity is then proportional to the number of atoms that

* Communicated by Prof. R. W. Wood.

† Phil. Mag., Aug. 1928, p. 352.

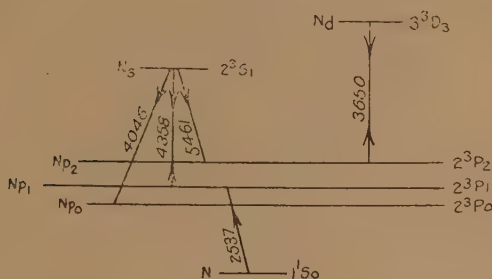
‡ R. W. Wood, Phil. Mag., Sept. 1927, p. 471.

happen to be excited in that level. This level is reached in our case of mercury vapour at room temperature, where the time between two collisions is large in regard to the life-time of an excited atom, so that collisions of the first or second kind do not play a significant role, only by the absorption of the line 3650 of the arc by the atoms on the level 2^3P_2 . We will call N_d , N_s , N_{p_1} , N , etc., the number of atoms in the different levels, as illustrated by fig. 1. N_d , the number of atoms in the level 3^3D_3 , is then proportional to N_{p_2} , and to the intensity of the line 3650 of the arc, that we will call I_{3650} or simply I_3 . It is then

$$N_d = c \cdot I_{3650} N_{p_2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is a constant factor that does not interest us for the moment.

Fig. 1.

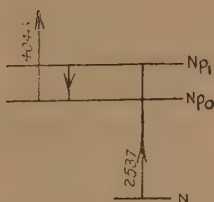


The level 2^3P_2 is supplied with electrons chiefly by the emission of the line 5461 by atoms with electrons on the level 2^3S_1 . The emission of 3341, 3663, 3654, and 3023 by the fluorescent vapour also brings electrons to that level (fig. 2), but the sum of the intensities of these lines in fluorescence is about 0.08 of the intensity of the green line 5461, so that one can neglect them in a first approximation. This is the reason why Wood found that only electrons coming down from 2^3S_1 seemed to be effective in producing the absorption and re-emission of 3650. The absorption of 4358 in the exciting light by means of a filter placed between arc and tube made 3650 practically disappear, in spite of the fact that 3131 and 3650 were not reduced by the filter*. The number of atoms on the level of 2^3P_2 is then proportional to the intensity of the green line in fluorescence that we will call J_{5461} . In general we will denote

* Phil. Mag., Oct. 1925, p. 786.

arc-line 2537 fall back to the normal level again, emitting that same line in resonance, and that only a small number of them are raised to higher levels owing to the absorption of 4358, 3131, 3125. Thus the total number of excited atoms in levels higher than 2^3P_1 is small in comparison with the number in this level. We can then calculate its density, neglecting the contributions from above. On the other hand, the number of normal atoms N is in all practical cases large in comparison with the sum of all the excited atoms, so that we can consider it as constant and independent of the intensity of the exciting light. One might think that this would be no longer true if we were able to increase the intensity of the arc sufficiently, especially considering the existence of metastable levels in which excited atoms might accumulate in such quantity as to diminish sensibly the amount of normal atoms. The following simple considera-

Fig. 3.



tions show that this cannot be the case; in fact, let us calculate the maximum amount of metastable atoms that can be obtained under ideal conditions.

If we assume that every atom excited by the absorption of 2537 becomes in one way or another, sooner or later, a metastable atom, the number of atoms falling to the level 2^3P_0 will be in the unit time $N\gamma I_{2537}$, where γ is the absorption coefficient of 2537. Let us also assume that atoms leave the level 2^3P_0 only because of the absorption of the line 4046; $\pi I_{4046} N_{p_0}$ is then the number of atoms leaving 2^3P_0 in the unit time, if π is the absorption coefficient of 4046. Under stationary conditions those two quantities must be equal, thus

$$N_{p_0} = N \frac{\gamma I_{2537}}{\pi I_{4046}}.$$

Now $\frac{I_{2537}}{I_{4046}} = 4$ in the arc, so that the ratio N/N_{p_0} is mainly determined by the ratio of the absorption coefficients of 4046

and 2537. This last ratio is not known, but one may safely assume that it is at least equal to 10. The ideal maximum number of metastable atoms can be then no more than $\frac{4}{10}$ of the amount of normal atoms,

$$\frac{N}{N_{p_0}} > 2.5.$$

In the practical case collisions of the second kind with impurities (H_2), and especially with the walls of the tube, and emission of the "forbidden line" 2656, will reduce the amount of metastable atoms, and thus increase considerably the ratio given above. N is then practically constant and the expression (3) is justified.

Summing up, we can write

$$N_d \sim I_3 \cdot N_{p_2} \sim I_3 \cdot N_s \sim I_3 \cdot I_2 \cdot N_{p_1} \sim I_3 \cdot I_2 \cdot I_1 \cdot N, \quad (4)$$

where I_1 , I_2 , I_3 are the intensities of the arc lines 2537, 4358, and 3650 respectively, and N , as said before, the number of normal atoms.

The intensity of the re-emission line 3650 will be

$$J_{3650} \sim N_d \sim I_1 I_2 I_3. \quad . \quad . \quad . \quad . \quad (5)$$

We must, however, consider the reduction of the intensity of the light of the arc by the vapour absorption as the rays traverse the tube. Owing to this, the intensity of the fluorescence may fall off appreciably along the diameter of the tube. Let us consider a volume element, v , in the interior of the vapour. Let its position be characterized by the coordinate x , measured from the entrance-point of the rays. The intensity of the lines 2537, 4358, and 3650 of the arc in the volume element v will be a function of x . The same is true for the fluorescence line 3650. We ought then to write

$$J_{3650}^{(x)} = A I_1^{(x)} I_2^{(x)} I_3^{(x)}, \quad . \quad . \quad . \quad . \quad (6)$$

where the exponents (x) will denote that those quantities are functions of x .

We can now answer the question set at the beginning of the paper. The intensity of the fluorescence line 3650 emitted by the volume element v will increase with the cube of the arc intensity as far as the intensities of the three arc lines concerned in its emission, *measured in the volume element* v , do really increase proportional to the intensity of the arc. We shall see that this is not always the case. To know how the primary intensities change with the position of the element v , we have to study the absorption laws for the different lines of the arc in the excited mercury vapour.

The Absorption of 2537 and of 4358.

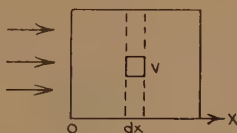
To simplify the calculations we will assume that our resonance tube is of square section, and that the exciting light is parallel. The position of a volume element v will be then characterized by its distance x from the entrance wall of the exciting light, and all of our quantities will be functions of that single variable.

The absorption law of 2537 is well known and reads

$$I_{2537} = I_0 e^{-\gamma x}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where I_0 is the intensity at the entrance wall of the tube, e is the basis of the natural logarithms, and γ is the absorption coefficient of the line which depends only on the density N of normal atoms in the vapour. At a given temperature of the saturated vapour that number will not depend on the intensity of the exciting light, as we saw above, and γ is then a constant.

Fig. 4.



To calculate the absorption of 4358 we need to know the number of atoms in the level 2^3P_1 as a function of x . The number of atoms raised to that level in the layer dx during the time l at the distance x of the entrance wall will be equal to

$$dI_1 = \gamma I_1 dx, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\gamma = cN$.

To that number we must add the number of atoms that fall from higher levels, but we have already seen that this number is small in comparison with the quantity raised by absorption of 2537, and we can, therefore, neglect them.

In the stationary state an equal number of atoms will abandon the level 2^3P_1 owing to spontaneous emission of the resonance line 2537, to absorption of lines like 4358 originating in that level, and to collisions of the first and second kind. If we call A , B , C , and D the probabilities of those four processes, the number of atoms leaving the level 2^3P_1 in the layer dx , and during the time unit, will be given by

$$N_{p1}(A + B + C + D)dx. \quad . \quad . \quad . \quad . \quad (9)$$

The mean life-time of an excited atom in that level will be then

$$\tau_{p_1} = \frac{1}{A+B+C+D} \quad . \quad . \quad . \quad . \quad (10)$$

We have already seen that collisions of the first or second kind do not come into consideration because of the low temperature and of the low pressure of the vapour (the mean time between two collisions is of the order of 10^{-4} sec.), and that experimental results show that the number of atoms raised by absorption to higher levels is small in comparison with the number of atoms falling back to the normal state by re-emission of the resonance line, which means that B, C, and D are small in regard to the probability A of spontaneous emission, and we can neglect them safely. We have, then, practically

$$\tau_{p_1} = 1/A \quad . \quad . \quad . \quad . \quad (11)$$

Equating (8) and (9), and considering (10) and (11), we have

$$N_{p_1} = \gamma \tau_{p_1} I_1 = \gamma \tau_{p_1} I^0 e^{-\gamma x} \quad . \quad . \quad . \quad . \quad (12)$$

If we consider the excited atoms as forming a different gas, we can say that we have a gas the density of which falls exponentially as we retreat from the entrance wall of the light. We could say that the partial pressure of the gas falls exponentially, but it is not safe to speak of a partial pressure in this case. In fact, pressure is a thing that is given only by collisions, and since the mean life of an atom in the level 2^3P_1 (10^{-7} sec.) is much shorter than the time between two collisions of the excited atom in a gas of a pressure of 0.001 mm. (about $2 \cdot 10^{-4}$ sec.), the definition of pressure loses here its meaning in this case. We can speak of the density of the excited atoms, but not of a partial pressure. For the same reason, in spite of the fact that we have a gradient of the density, no diffusion will take place from the regions of higher to the regions of lower density. The path that an excited atom traverses during its mean life is only of the order of 10^{-3} cm. We shall see later that in the case of the metastable levels diffusion must be taken into account.

Now that the density distribution in the level 2^3P_1 is known, one can go a step farther and reckon the absorption of 4358. The absorption coefficient for this line will be proportional to the number of excited atoms, in the same way as the absorption coefficient of 2537 was proportional to the number of normal atoms. The difference is that in

the former case the coefficient was constant, while here it is a function of x . We can then write

$$dI_{4358} = -\delta I_{4358} dx, \quad . \quad . \quad . \quad (13)$$

where

$$\delta = aN_{p_1} = a\gamma\tau_{p_1}I_1^\circ e^{-\gamma x}.$$

We set

$$\alpha = a \cdot \gamma \cdot \tau_{p_1}, \quad . \quad . \quad . \quad (14)$$

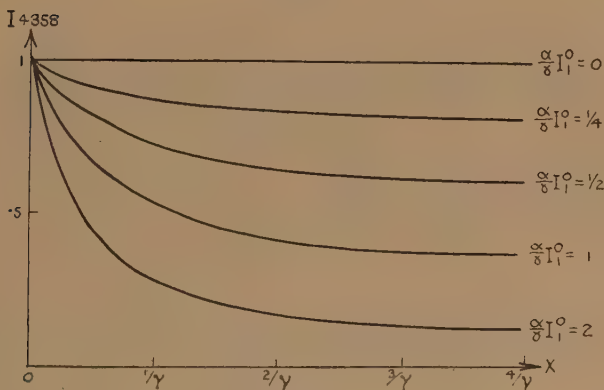
and (13) becomes

$$dI_2 = -\alpha I_1^\circ \cdot e^{-\gamma x} \cdot I_2 \cdot dx. \quad . \quad . \quad . \quad (15)$$

The integral of this expression is

$$I_{4358} = I_2 = p \cdot e^{-\alpha \cdot I_1^\circ \cdot \int_0^x e^{-\gamma x} \cdot dx} = p \cdot e^{\frac{\alpha}{\gamma} \cdot I_1^\circ \cdot e^{-\gamma x}}.$$

Fig. 5.



The constant p is given by the condition that for $x=0$, $I_2 = I_2^\circ$ to

$$p = I_2^\circ e^{-\frac{\alpha}{\gamma} I_1^\circ (1 - e^{-\gamma x})}.$$

We have then

$$I_{4358} = I_2^\circ \cdot e^{-\frac{\alpha}{\gamma} I_1^\circ (1 - e^{-\gamma x})} \quad . \quad . \quad . \quad (16)$$

This expression can be abbreviated to

$$I_2 = I_2^\circ \cdot e^{-\frac{\alpha}{\gamma} (I_1^\circ - I_1)} \quad . \quad . \quad . \quad (17)$$

This is the absorption law for 4358. The same law will govern the absorption of 2894, 3131, 3125, 2652, 2654, 2655, and 4077.

Fig. 5 illustrates formula (17) for different values of $\frac{\alpha}{\gamma} I_1^\circ$. I_2° is set = 1.

The constant α plays in regard to 4358 a similar rôle as γ in regard to 2537. In that sense α could be called the absorption coefficient of 4358. The numerical value of α can be obtained by measuring the absorption of 4358 for a given value of x . Actually the absorption of 4358 is very small, and the line appears without a trace of reversal if examined with the large Lummer-Gehrke plate after traversing a 10 cm. layer of strongly excited vapour. That means that $\frac{\alpha}{\gamma} I_1^\circ$ is small, and that I_2 is practically constant and equal to I_2° all along the cross-section of the tube. This would no longer be the case if we were able to increase sufficiently the intensity of 2537 (I_1°).

The Number of Atoms on the Level 2^3S_1 .

Now that we know the absorption law of 4358 we can calculate the density distribution on the level 2^3S_1 , which will enable us to reckon the intensity of the fluorescence line 5461 in order to calculate the absorption of 3650. The absorption of 4358 in the layer dx at the distance x during unit time will bring a number

$$dI_2 = \alpha \cdot I_2 \cdot I_1 \cdot dx = \frac{1}{a} \cdot I_2 \cdot N_{p_1} \cdot dx \quad . \quad . \quad (18)$$

of atoms to the level 2^3S_1 . By emission of the triplet 4046, 4358, and 5461 these atoms will leave 2^3S_1 and distribute themselves among the three 2^3P levels. Now the upper and the lower of these levels are metastable, and the mean life of atoms on them, as measured by Dorgelo*, is of the order 10^{-3} sec. at least. We shall see later that we can confirm this result. Due to this long life, atoms will accumulate in the metastable levels, and if they do it in sufficient numbers they will absorb on their part the lines 4046 and 5461 of the arc, and thus bring a new contingent of atoms to the level 2^3S_1 . We cannot know *a priori* in which way most of the atoms reach that level, but we can make the following consideration:—If most of the atoms that reach 2^3S_1 are due to the absorption of 4358, the intensity of the re-emission lines 4046, 4358, and 5461 must be proportional to the square of the intensity of the exciting light, because two successive absorptions would be needed. On the other hand, if most of the atoms on that level were due to the absorption of 4046 or 5461 by the metastable

* *Physika*, vol. v. p. 435 (1925).

atoms, we would need three successive absorptions (absorption of 2537, absorption of 4358, emission of 4046 and 5461, and absorption of 4046 and 5461), to reach that level, thus the intensity of the re-emission lines ought to be proportional to the cube of the arc intensity. It has been found experimentally that the lines in question change with the square of the primary intensity, which shows that only the absorption of 4358 is of importance for the supply of electrons to the level 2^3S_1 .

We do not need then to consider the re-absorption by the metastable atoms.

The number of atoms that leave the level 2^3S_1 in the layer dx and during the time unit will be

$$N_s \frac{1}{\tau_s} dx, \quad (19)$$

if τ_s is the mean life-time of that level. In the stationary state the quantities (18) and (19) must be equal, and we have

$$N_s = \alpha \cdot \tau_s \cdot I_1 \cdot I_2. \quad (20)$$

This gives us the density distribution on the level 2^3S_1 . The intensities of the lines emitted by that level will be given by the same expression multiplied with the numerical factor corresponding to the transition probability of each of the three lines. It is then

$$J_{5461} = \epsilon_2 N_s, \quad J_{4358} = \epsilon_1 N_s, \quad J_{4046} = \epsilon_0 N_s, \quad . . . (21)$$

where
$$\epsilon_0 + \epsilon_1 + \epsilon_2 = \frac{1}{\tau_s}.$$

Let us consider more closely one of these expressions, for instance, J_{5461} . Its intensity is by formulæ (20) and (21) proportional to the product of the intensities of two lines of the arc, 2537 and 4358. I_{2537} is an exponentially falling curve (formula 7), and its intensity will increase everywhere in the same ratio if we increase the light of the arc. I_{4358} is practically constant along the cross-section of the tube because the absorption of that line is weak, as we saw above. The product of both curves will give again, then, an exponentially falling curve with an extinction coefficient equal to the absorption coefficient of 2537. We should, therefore, expect that the intensity distribution of the fluorescence line 5461 along the cross-section of the tube will be given by an exponential function with an exponent coefficient γ . This can be tested experimentally. If we form an image of the cross-section of the tube upon the slit

of the spectrograph (see fig. 13 in the following paper) by means of a long-focus quartz achromatic lens, as described by Wood in one of his former papers, the intensity at the top of the slit will correspond to the light emitted by the layers at the entrance wall of the tube, while the intensity at the bottom of the slit will originate in the layers near the exit wall of the tube. Wood (*l. c.*) has already published a photograph of the lines 3654, 3663, and 3650 taken in that way, which shows that the experiment confirms our theory. A quantitative agreement cannot be expected, because in the experimental case the exciting light is not parallel, as assumed in our calculations, but divergent. The divergence of the intensity is probably proportional to the distance or less, and not to the square of the distance, because the light-source is long (10 cm.) and has a thickness of about 1 cm.

Expressions similar to (20) will give the density distribution of excited atoms in all the levels that are reached after two successive absorptions, like 2^1S_0 , 3^3S_1 , 3^1D_2 , 3^3D_1 , 3^3D_2 , and so forth, and expressions similar to (21) the intensity of the lines emitted by them.

The Number of Atoms in the Level 2^3P_2 .

The last expression for the intensity of the green line 5461 in fluorescence, or better, the differential of that expression, gives us the number of atoms that in the layer dx and unit time fall to the level 2^3P_2 . As we saw at the beginning, the emission of other lines like 3654, 3663, etc., brings also atoms to that level, but their quantity is negligible in comparison with the quantity brought down by the green line.

Because of the long life of the metastable level we should expect that the atoms falling to it (the density of which, as a function of x , is practically given by an exponential curve) would diffuse in the tube, so that they would distribute themselves homogeneously all over the cross-section of it. If that should take place, the absorption of 3650 would be constant along the section of the tube (3650 of the arc is absorbed very little in 2 cm. vapour, so that I_{3650} is practically constant), and the re-emission line 3650 should be also of constant intensity along the cross-section of the tube. Experiments show that this is not the case. The intensity distribution of 3650 along the slit of the spectrograph is the same as that of 4358 or 3654. That seems to show that diffusion does not take place in the level 2^3P_2 under our

conditions, which signifies that the life of that level cannot be longer than 10^{-5} sec. The reasons for the shortening of the life of the metastable atoms on that level are probably to be sought in the absorption of the green line of the arc. If we remember formula (10) we see that the mean life of an excited level is inversely proportional to the sum of emission, absorption, and collision probabilities. Here the spontaneous emission probability is nearly equal to zero, and the collision probabilities are small, but the absorption probability for the lines originating on our level seems to be sufficiently large to shorten the life of the metastable level by the amount necessary to avoid diffusion*. We can thus go on in our calculation without considering it.

The number of atoms that reach 2^3P_2 in the layer dx is

$$J_{5461} dx. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The number of atoms that leave it is

$$N_{p_2} \frac{1}{\tau_{p_2}} dx. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Therefore

$$N_{p_2} = \tau_{p_2} \cdot J_{5461}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This gives the density distribution in 2^3P_2 and enables us to calculate the absorption of 3650.

The Absorption Law of 3650.

The absorption coefficient of 3650 is given now by

$$\frac{dI_3}{I_3} = b \cdot N_{p_2} \cdot dx = \omega \cdot \alpha \cdot I_1 \cdot I_2 \cdot dx, \quad . \quad . \quad (25)$$

where

$$\omega = b \epsilon_2 \tau_{p_2} \tau_s.$$

The integration of this expression gives as a result

$$I_{3650} = I_3 = I_3^0 e^{-\omega I_2^0 \left[1 - e^{-\frac{\alpha I_1^0 (1 - e^{-\gamma x})}{\gamma}} \right]} = I_3^0 e^{-\omega (I_2^0 - I_2)}. \quad (26)$$

This is the absorption law for 3650. This equation looks very complicated, but in the experimental case ω is small; thus I_3 is practically constant and equal to I_3^0 .

The density distribution in the level 3^3D_3 will be then given by

$$N_d = \omega \alpha \tau_d I_1 I_2 I_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

* Meissner and Graffunder (*Ann. d. Phys.* lxxxiv. p. 1009 (1927)) have found that side radiation is able to shorten the life of the metastable levels of Neon and Argon from 2 to 5 times.

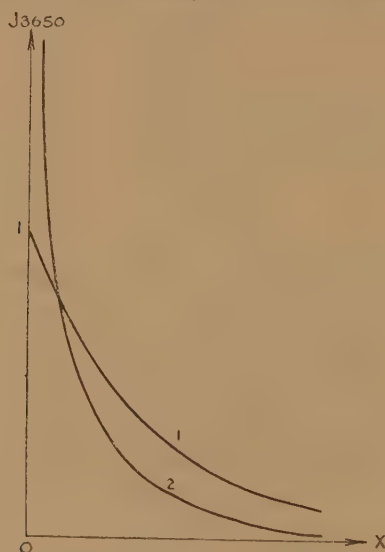
and the intensity of the fluorescence line 3650 by

$$J_{3650} = \frac{N_d}{\tau_d} = \omega \alpha I_1 I_2 I_3 = \omega \alpha I_1^{\circ} \cdot I_2^{\circ} \cdot I_3^{\circ} e^{-\gamma x} \cdot e^{-\frac{\alpha}{\gamma}(I_1^{\circ} - I_1)} \cdot e^{-\omega(I_2^{\circ} - I_2)} \quad (28)$$

Discussion of the Intensity Question.

We are now able to state what will happen in each volume element of the resonance tube if we increase constantly the intensity of the exciting light. We have already seen that in the actual case the two last factors of

Fig. 6



formula (28) are practically equal to one, thus the intensity distribution of 3650 as a function of x will be determined by $e^{-\gamma x}$, and its intensity will increase in every part of the tube proportional to the product of $I_1^{\circ} \cdot I_2^{\circ} \cdot I_3^{\circ}$, or, if we assume that the ratio $I_1^{\circ} : I_2^{\circ} : I_3^{\circ}$ is constant in the arc, proportional to the cube of the intensity of the arc. Fig. 6, curve 1, represents J_{3650} for this case. If we are able to increase the arc intensity sufficiently, the last two factors of the formula (28) would no longer be equal to one, but they would be more and more rapidly falling curves. J_{3650} would then be equal to the product of three falling curves, and could be represented by the curve 2 of fig. 6. We see that

the intensity of 3650 would still increase proportional to the cube of the arc intensity only in the first layer by $x=0$, but would eventually *decrease* for larger values of x . This means physically that the volume fluorescence of 3650 would concentrate more and more at the entrance wall of the tube, and we should have a thing similar to surface fluorescence. We cannot realize experimentally this case for the Hg fluorescence *in vacuo*, because we are not able to increase sufficiently the intensity of the arc, but we can do it by admitting gases into the tube, as we shall see in the following paper. The admission of 2 mm. water vapour, for instance, increases 4358 about 20 times for small x , but actually decreases it for larger values of x . (See Theory II.)

Summary.

The intensity of the different lines of mercury vapour at room temperature when excited optically by a water-cooled mercury arc has been calculated as a function of the primary intensities, and of the position of the emitting volume element in the tube, and the results allow us to understand the special behaviour of some lines like 3650.

The absorption laws for lines like 4358 and 3650 in excited mercury vapour have been calculated.

It is a pleasure for the author to acknowledge his indebtedness to Professor R. W. Wood for his many advices and assistance during the present work, and to Professor K. F. Herzfeld, who was so kind as to read this paper in manuscript and to suggest several improvements.

The Johns Hopkins University,
Baltimore, Md.
June 30, 1928.

CXV. *The Influence of Foreign Gases on the Optical Excitation of Mercury.*—Theory II. By E. GAVIOLA, Ph.D., Fellow of the International Education Board*.

[Plates XXV. & XXVI.]

IN the course of his extensive investigation of the fluorescence of mercury vapour, excited by the light of a water-cooled, magnetically deflected, mercury arc, Wood † has

* Communicated by Prof. R. W. Wood.

† Wood, Phil. Mag., Oct. 1925, Sept. 1927.

found that the admission of other gases to the tube containing the fluorescing mercury vapour at a pressure of 0.001 mm. (saturated vapour at room temperature) produced various effects upon the different remission lines, depending on the nature of the particular gas and on the partial pressure of it in the tube. It was found, for instance, that nitrogen at pressures of from 0.05 to 0.4 mm. decreased several times the intensity of the line 3650, while higher pressures up to 6 or more mm. increased it considerably. At 3 mm. it decreased the lines 3654, 3125, 4077, 2537, 3021, and at the same time enhanced many others like 5461, 4358, 4046, 3131, 3341, 2654, 2535. Carbon monoxide at low pressures decreased 3650, 3654, 3125, 3021, etc., and increased 3341, 3131, 2653, 2534, etc. Argon and helium behave similarly. Wood has also found that many of these changes can be explained if we assume that the collisions with molecules of the foreign gases bring a large number of atoms to the metastable level 2^3P_0 , where they accumulate due to the stability of that level, and become capable of absorbing strongly the line 4046 of the arc, practically not absorbed without the foreign gas; and he showed the existence of this absorption by photographing the 4046 line of the arc, after traversing a layer of excited vapour, with the large quartz Lummer-Gehrke plate, with the result that it appeared strongly reversed when nitrogen was present, but not in its absence. During the present work the action of different gases upon the absorption of 4046 has been studied in detail. This study has brought new and interesting facts to light in regard to the diffusion and lifetime of the metastable atoms and to the efficiency of their collisions with different gases—facts that enable us to calculate and predict the behaviour of the lines, especially the intensity distribution along the cross-section of the tube and its change when gases are admitted.

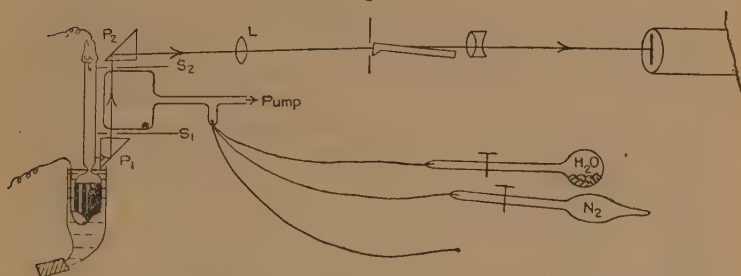
The Absorption of the Line 4046.

The arrangement used was similar to that used by Wood (*l. c.*), and is shown schematically by fig. 8.

A very clear and large quartz tube, 10 cm. long and 10 cm. in diameter, with plane end-surfaces was illuminated by the magnetically-deflected light of the water-cooled mercury arc, a part of which light was received by the quartz prism P_1 and sent parallel to the illuminated wall of the tube through the excited mercury vapour. A second quartz prism P_2 sent the light to the lens L of fused quartz, which made it parallel or slightly convergent to allow it to enter the large quartz

Lummer-Gehrke plate after traversing a polarizer. A quartz-fluorite achromat of 42.5 cm. focal distance threw an image of the interference system upon the wide open slit of the spectrograph. Two screens S_1 and S_2 limited the light-beam, and could be displaced so as to make the beam traverse the vapour at different distances from the entrance wall of the exciting light. The tube was in connexion with the pump and with bulbs containing the desired gases. A very fine capillary was occasionally used for admitting air or oxygen. Series of photographs of the line 4046 were taken with different pressures of CO, water vapour, and nitrogen in the tube. Fig. 1 (Pl. XXV.) shows the results. The first horizontal series corresponds to CO at partial pressures 0, .015, .1, .35, and 4 mm., the second to water vapour at pressures 0, .005, .03, .1, 1.5 mm., and the third to nitrogen at 0, .13, .55 mm. All the photographs had the same time

Fig. 8.



of exposure, 4 minutes. We can see that the presence of 0.015 mm. CO is sufficient to show a clear reversal of the main component (indicated by an arrow) of the line. If we increase the pressure, the reversal increases up to 0.1 to 0.2 mm. CO, and decreases again at higher pressures. At 4 mm. the reversal has disappeared completely, and no traces of absorption are left. Water vapour shows a trace of reversal at 0.005 mm., which increases rapidly by increasing water-vapour density until at 1 to 2 mm. the whole line is practically absorbed. At low pressures the behaviour of CO and H_2O is practically the same. Above 0.2 mm., on the contrary, the absorption of 4046 diminishes with CO, while it still increases with H_2O . We shall see later on that the theory is able to explain this fact on the assumption that the collisions of the second kind of metastable atoms with CO are more efficient than with H_2O . On the other hand, N_2 shows no clear reversal until a pressure of about 0.5 mm. is

reached ; but a diffuse absorption of the line takes place from 0.1 mm. up, showing that in the presence of nitrogen not only the core of the line is absorbed, but the whole line, which seems to mean that nitrogen is capable of broadening the absorption line 4046. At higher pressures N_2 behaves similarly to H_2O , but water seems to be still more efficient than N_2 in accumulating atoms in the lower metastable level.

It was of importance to determine if a diffusion of the metastable atoms takes place. Metastable atoms are mostly generated at the entrance wall of the exciting light, because of the strong absorption of the resonance line in the mercury vapour at room temperature. A layer of 5 mm. reduces 2537 to $\frac{1}{2}$ of its original value ; thus at 2 cm. distance of the entrance wall its intensity is only $\frac{1}{16}$. Now, the number of metastable atoms generated in each volume element of the tube, as we shall see later, is proportional to the intensity of the line 2537 of the arc at that volume element. If diffusion of the metastable atoms does not take place, the absorption of the line 4046 should decrease 16 times if the light-beam traverses the tube at a distance of 2 cm. from the illuminated wall of the tube ; which amounts to saying that the absorption should practically disappear. On the other hand, if the metastable atoms live so long as to diffuse all along the cross-section of the tube, the absorption of 4046 should be the same everywhere. To test this point the screens S_1 and S_2 (see fig. 8) were so placed as to make the beam of light traverse the tube parallel to the illuminated wall at distances of 2 and 5 cm. from it. Fig. 2 (Pl. XXV.) shows the result of a series of photographs taken with different pressures of water vapour in the tube, and with the beam traversing it at 2 cm. distance from the illuminated wall. We see that *in vacuo* no reversal takes place, as is to be expected, but a clear reversal of the main component of the line (indicated with arrows) appears with 0.2 to 0.5 mm. water in the tube, to disappear again if the pressure attains 2 mm. If the beam traverses the tube at 5 cm. distance from the wall, no reversal is to be detected under any water pressure. These facts show that diffusion of the metastable atoms does actually take place at low water pressure, and that the mean life of the excited atoms is long enough to allow them to diffuse 2 cm., but not long enough to allow them to diffuse 5 cm. With these values we shall make, in a following paragraph, an approximate calculation of the mean lifetime of a metastable atom on the level 2^3P_0 .

The reason why the diffusion disappears if the water pressure is increased to 2 mm. is probably two-fold : the

higher pressure shortens the mean life of the metastable atoms, and, on the other hand, the diffusion velocity diminishes with the pressure, so that in the case in which the mean life is not decreased, the path travelled during that life would diminish in proportion to the pressure.

The same experiments were repeated with N_3 , with the result that no reversal of 4046 could be found at 2 cm. distance with any nitrogen pressure. This result is to be expected because we have already seen that, with N_2 , when the beam traverses the tube close to the illuminated wall, the reversal begins at the pressure of 0.5 mm., which is already too high to allow them to diffuse. No diffusion experiments have been made with CO so far, but I should expect it to behave at low pressures like water vapour.

The Metastable Level 2^3P_2 .

These experiments show that large quantities of atoms accumulate on the metastable level 2^3P_0 . Now, mercury has another metastable level, the level 2^3P_2 . It was of importance to ascertain if atoms accumulate in this level also. To examine this question, the lines 5461 and 3650 of the arc were photographed as before, to see if they reverse when gases are introduced. The result was that no reversal or absorption of 5461 could be detected under any conditions. This proves that the upper metastable level must be many times less densely occupied than the lower one in the presence of gases. On the other hand, Wood has observed that the arc line 3650 appears slightly reversed if it traverses a 10 cm. long layer of excited mercury vapour in the absence of any gases. I can confirm this result. Now, if we introduce gases into the tube, the reversal at first disappears (gases at low pressure), to come up again if we attain a water or nitrogen pressure of 1 or 2 millimetres, which shows that the number of atoms in 2^3P_2 decreases at first to increase afterwards. The change of the intensity of the fluorescence line 3650 is in accordance with this result. Its intensity can be given by the formula

$$J_{3650} = a \cdot I_{3650} \cdot N_{P_2},$$

where I_{3650} is the intensity of the arc line 3650, and N_{P_2} is the density of atoms on the level 2^3P_2 (see preceding publication: Theory I., formula (1)). Now, the introduction of gases at low pressure does not change I_{3650} of the arc, so that the changes in the intensity of the remission line 3650 are, so to speak, a measure for the changes in the density of

atoms on the level 2^3P_2 . In fact, at foreign gas pressures below 1 mm. the time between two collisions of an excited Hg atom is larger than 10^{-7} sec., so that collisions of the second kind play a rôle only in regard to the 2^3P levels, the mean life of which is longer than this time. All the other levels will be practically undisturbed by collisions. Wood has already measured the changes in the intensity of the fluorescence lines with different pressures of nitrogen. The following is an abstract of his measurements :—

Nitrogen pressure .	1.25	0.43	0.2	0.1	0.05	0.00 mm.
5461	12	6	4	2	1.5	1
3650	1	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{5}$	$\frac{1}{8}$
<u>5461</u> <u>3650</u>	12	6	8	8	$7\frac{1}{2}$	1

We see in the second line that the intensity of 3650 decreases at first and increases slowly afterwards with growing pressures of nitrogen, while 5461 increases steadily (the initial intensities are arbitrarily set equal). Now, we have seen that the level 2^3P_2 is supplied with electrons practically exclusively by the emission of 5461 (Theory I.). The increase of that line means an increase in the number of atoms that reach that level. In spite of this fact the number of atoms in the level diminishes as shown by the intensity of 3650. The density of atoms on 2^3P_2 can diminish only as a result of collisions with the nitrogen molecules. The ratio of the increase of 5461 to the increase of 3650 will give the number of times that the density in the level 2^3P_2 decreases due to the collisions. That ratio is given above. We should expect the ratio to grow with the pressure. It grows with it, but in an irregular way. But we must remember that Wood considered the given values as provisional. In that light the result can be regarded as satisfactory. The level 2^3P_2 seems, then, to be very sensitive to collisions with nitrogen molecules. The fact that 0.1 mm. of nitrogen is able to diminish 8 times the number of atoms in 2^3P_2 is very remarkable if we remember that the same gas pressure would quench the re-emission line 2537 only to about 97 per cent. of its original value (see the known quenching curves of Stuart), which means that the number of atoms on the level 2^3P_1 is only very slightly decreased. We have here the interesting case in which a "metastable level" becomes much less stable against collisions than an "unstable level." This may be correlated with the fact that Lord Rayleigh has observed the "forbidden" line 2270, which is emitted by the level 2^3P_2 in both emission and absorption.

The extremely great sensibility of the excited atoms in the level 2^3P_2 to collisions is not only shown in regard to nitrogen, but to all the other gases that have been tried.

We can make a rough calculation of the mean life of the atoms in the metastable level 2^3P_2 on the base of the facts outlined above. The number of atoms in the level 2^3P_2 is given by formula (24) of Theory I. :

$$N_{P_2} = \tau_{P_2} \cdot J_{5461}.$$

This relation is true for every gas pressure. We can plot now J_{5461} and N_{P_2} as function of the pressure if we admit J_{3650} as a measure for N_{P_2} . The division of both curves gives us the mean life τ_{P_2} as a function of the pressure. The

Fig. 9.

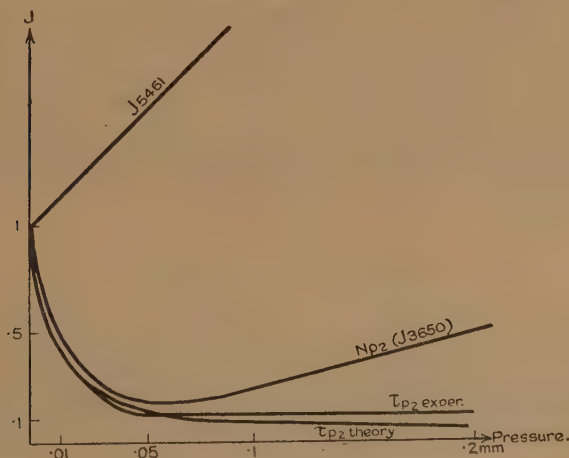


diagram (fig. 9) shows that τ_{P_2} decreases with the pressure, which is to be expected. At 0.01 mm. nitrogen τ_{P_2} decreases to $\frac{1}{2}$ of its original value. The time between two collisions of an excited atom at that pressure of nitrogen is about 10^{-5} sec.

Now
$$\tau_{P_2} = \frac{1}{B_2 + D_2}$$

if B_2 is the absorption and D_2 the collision probability, and if we neglect the emission probability. On its side $D_2 = ZE_2$ if Z is the number of collisions and E_2 the efficiency of them ; hence

$$\tau_{P_2} = \frac{1}{B_2 + ZE_2} \cdot \cdot \cdot \cdot (29)$$

This value will decrease to $\frac{1}{2}$ when the pressure is such that $B_2 = ZE_2$. Experimentally it does so at 0.01 mm. pressure, at which $Z=10^5$ collisions per sec. That means $B_2=10^5 \cdot E_2$, and for $Z=0$:

$$\tau_{P_2} = \frac{1}{B_2} = 10^{-5} \cdot E_2 \text{ sec.}$$

If every collision is effective ($E_2 = 1$), 10^{-5} sec. is the mean life of the metastable level 2^3P_2 for the case of vacuo; that is, when no foreign gas is present. If gases are admitted, τ_{P_2} decreases according to formula (29). In fact, if we plot (29) according to the value given above, we obtain the lower curve of fig. 9, which is in surprisingly good agreement with the empiric curve for τ_{P_2} .

Summing up, we can say that the primary and principal action of gases consists in bringing excited atoms from the levels 2^3P_2 and 2^3P_1 to the metastable level 2^3P_0 . If the gas pressure is sufficiently low, diffusion of the metastable atoms takes place; otherwise not. We will now see that the theory enables us to explain all the other changes due to gases, especially the changes in the distribution of the intensity along the cross-section of the tube, without making further assumptions.

The Levels 2^3P_1 and 2^3P_0 .

We have seen in the first part of this investigation (Theory I., formula (12)) that the density distribution of atoms on the level 2^3P_1 in the case of vacuo, that is, in the case when only Hg vapour at room temperature is in the tube, was given by the formula

$$N_{P_1} = \gamma \tau_{P_1} I_1^0 e^{-\gamma x}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where γ is the coefficient of absorption of the resonance line 2537 of the arc, τ_{P_1} the mean life of an excited atom on the level 2^3P_1 , and x the distance of the volume element considered from the illuminated wall of the tube. This formula holds also for the case of gases with the sole difference that τ_{P_1} was determined *in vacuo* practically exclusively by the emission probability A_1 of the line 2537 (see formula (11), Theory I.), and it was $\tau_{P_1} = 1/A_1$, while now the mean life is shortened by the collisions with the gas molecules that bring atoms to the lower level 2^3P_0 . It is now

$$\tau_{P_1} = \frac{1}{A_1 + D_1}, \quad . \quad . \quad . \quad . \quad . \quad (29')$$

where D_1 is the probability that a collision of the second kind will take place, which is given by the number of collisions in the time unit multiplied with the efficiency E_1 of those collisions in producing transitions without radiation:

$$D_1 = z \cdot E_1 \cdot \dots \dots \dots (30)$$

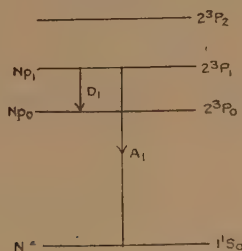
z is proportional to the gas pressure.

The number of atoms in the layer dx , which during unit time will reach the metastable level 2^3P_0 because of collisions, will be

$$D_1 N_{P_1} dx.$$

Another contingent of atoms will reach the level 2^3P_0 because of the emission by the fluorescent vapour of lines like 4046, 2967, etc. (see fig. 2, Theory I., p. 1156); this contingent is

Fig. 10.



but negligible compared with the amount of metastable atoms produced by collisions. If no diffusion takes place, the number of atoms that will in unit time leave that level in the layer dx will be

$$N_{P_0} \cdot \frac{1}{\tau_{P_0}} \cdot dx,$$

where τ_{P_0} is the mean life duration of the metastable atoms. Equating these expressions, we have

$$N_{P_0} = \tau_{P_0} \cdot N_{P_1} \cdot D_1 = \pi \gamma I_1 = \pi \gamma I_1^0 e^{-\gamma x} \quad (31)$$

if we set

$$\pi = D_1 \cdot \tau_{P_1} \cdot \tau_{P_0}, \quad \dots \dots \dots (31')$$

and put for N_{P_1} its value given above. The mean life τ_{P_0} of the metastable level was determined in the case of vacuo mainly by the absorption of lines terminating on that level, and by the collisions with the walls of the tube. In our

case, the collisions of the second kind with gas molecules will play an important rôle. We can write

$$\tau_{P_0} = \frac{1}{A_0 + B_0 + D_0},$$

where A_0 is the emission probability of the forbidden line 2656, which is emitted by the metastable atoms, B_0 the absorption, and D_0 the collision probability. Now, the emission probability of the forbidden line is extremely low; thus we can practically put

$$\tau_{P_0} = \frac{1}{B_0 + D_0} \quad . \quad . \quad . \quad . \quad (32)$$

D_0 will be given by the number of collisions of the metastable atoms multiplied with the efficiency of those collisions:

$$D_0 = z \cdot E_0.$$

The numerical values of E_0 are not as well known as for the case of the level 2^3P_1 . According to results of Donat*, Dorgelo†, Loria‡, Franck and Cario§, and ourselves, E_0 is very large for H_2 , O_2 , small for CO , N_2 , He , and smaller still for Ar and H_2O . Quantitative determinations have not yet been made so far as I know.

Diffusion of Metastable Atoms.

Formula (31) was calculated under the assumption that no diffusion takes place, which, as we have seen, is not the case for gases at low pressure. The diffusion will not affect the total number of metastable atoms in first approximation, since it does not alter D_1 nor τ_{P_0} . It influences only the density distribution in the section of the tube. If we assume that in the case of diffusion the density becomes constant, which is not completely true in the experimental case, as we saw before, but very nearly realized, the average density will be

$$\bar{N}_{P_0} = \int_0^1 N_{P_0} dx$$

if 1 is the length of the cross-section of the tube. The integration gives as result

$$\bar{N}_{P_0} = \pi I_1^0 (1 - e^{-\gamma}) = \phi \cdot I_1^0, \quad . \quad . \quad . \quad (33)$$

where $\phi = \pi(1 - e^{-\gamma})$.

* Donat, *Zeits. f. Phys.* xxix. p. 345 (1924).

† Dorgelo, *Physika*, v. p. 435 (1925).

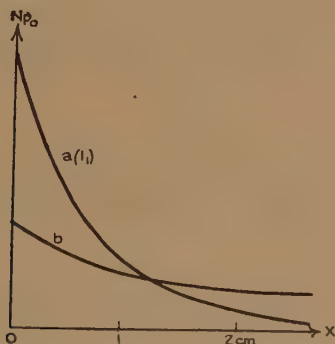
‡ Loria, *Phys. Rev.* xxvi. p. 573 (1925).

§ Franck & Cario, *Zeit. f. Phys.* xvii. pp. 202, 223 (1923).

The average density will thus be simply proportional to the total absorption of the line 2537 of the arc.

We can test formulas (31) and (33) by means of the "forbidden" line 2656. This line is emitted by the metastable atoms, and its intensity distribution along the cross-section of the tube will show directly the density distribution of the metastable atoms. Fig. 3 (Pl. XXVI.) gives a $6\times$ enlargement of two photographs of the forbidden line 2656 (on the long wave-length side of the pseudo-triplet 2652, 2654, 2655) taken while an image of the cross-section of the tube was thrown upon the slit of the spectrograph so that the light at the top of the slit corresponds to the emission near the entrance wall of the resonance tube ($x = 0$), and at the bottom to light near the exit wall ($x = 1$). a was taken

Fig. 11.



while 2 mm., b while 0.2 mm. water vapour were in the tube. We see that, in the first case, the intensity of 2656 decreases along the slit, while in the second it remains practically constant, as is to be expected after formulæ (31) and (33). The behaviour of the other lines will be explained later. The verification of our formulæ shows again that diffusion of the metastable atoms takes place with 0.2, but not with 2 mm. water vapour in the tube.

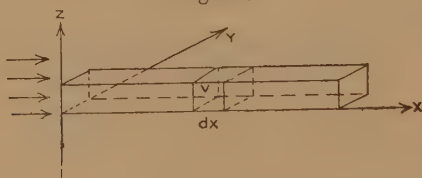
The Mean Life of the Metastable Atoms in the Level 2^3P_0 .

We saw in a former paragraph that when 2 mm. of water vapour are present in the tube, diffusion of the metastable atoms does not take place. The density distribution along the cross-section of the tube is given by the absorption law of the resonance line 2537, as shown by formula (31) and by fig. 11 (curve a). If we diminish the pressure, diffusion does

take place, and the density of the N_{P_0} atoms will be represented by a curve like b . The form of the curve b will depend on the mean lifetime of the metastable atoms, and on the diffusion-coefficient, which at a given temperature is inversely proportional to the pressure, and can be calculated with the help of the kinetic gas theory. Curve b will depend, then, at a given pressure, only on the mean life τ_{P_0} of the metastable atoms; for growing τ_{P_0} it will approximate to a horizontal line, and for small τ_{P_0} it will coincide with curve a . Now, curve b can be experimentally determined by measuring the absorption of 4046, or the intensity of the "forbidden" line 2656, for different x -values, and that will allow us to calculate the mean lifetime τ_{P_0} .

Let us consider a parallelepipedon of section $dy dz$ along the x -axis, which is perpendicular to the light entrance-wall of the tube (fig. 12), and a volume element $v = dx dy dz$ at the distance x of that wall, in which N metastable atoms are present. The number of metastable atoms that enter this

Fig. 12.



volume element in the time unit will be equal to the number of atoms diffusing from the left through the section x , that is,

$-D dy dz \frac{dN}{dx}$, where D is the diffusion-coefficient, plus the

amount produced in the volume v by the absorption of 2537 and successive collisions of the second kind, which, as we have seen (formula (31)), is proportional to the intensity of I_{2537} in the volume v , and it is $= v \cdot G e^{-\gamma x}$, where G is a factor which

is constant for a given pressure. $-D dy dz \left(\frac{dN}{dx} + \frac{d^2 N}{dx^2} \cdot dx \right)$

atoms will leave v diffusing through the section at $x + dx$, and a fraction $v \cdot N/\tau$ of the metastable atoms N in the volume v will die because of collisions of the second kind.

In the stationary state

$$-D dy dz \frac{dN}{dx} + v G e^{-\gamma x}$$

$$= -D dy dz \left(\frac{dN}{dx} + \frac{d^2 N}{dx^2} \cdot dx \right) + \frac{N}{\tau} dx dy dz$$

or

$$(a) \quad D \frac{d^2 N}{dx^2} - \frac{N}{\tau} + G e^{-\gamma x} = 0.$$

This is the differential equation of our curve *b*.

It is non-homogeneous and linear. The general solution of the homogeneous equation is

$$N = A e^{-x \sqrt{\frac{1}{\tau D}}} + B e^{x \sqrt{\frac{1}{\tau D}}},$$

and a special solution of the non-homogeneous one is

$$N = H e^{-\gamma x} \quad \text{if} \quad H = \frac{G \tau}{1 - \tau D \gamma^2}.$$

The sum of both expressions gives us our general solution

$$N = A e^{-x \sqrt{\frac{1}{\tau D}}} + B e^{x \sqrt{\frac{1}{\tau D}}} + H e^{-\gamma x}.$$

The boundary conditions are $N = N^0$ for $x = 0$, and $N = 0$ for $x = \infty$, which makes $B = 0$ and $A = N^0 - H$, and we obtain finally

$$(b) \quad N = (N^0 - H) e^{-x \sqrt{\frac{1}{\tau D}}} + H e^{-\gamma x}.$$

This is the density distribution of the metastable atoms as a function of x for given values of τ and D (curve *b* of fig. 11). N is equal to the sum of two exponential falling curves with different coefficients of extinction. The last term, which is originated by the absorption of 2537, decreases very rapidly, and will fall already to $\frac{1}{8}$ of its original value for $x = 1.5$ cm. (2537 is reduced to $\frac{1}{2}$ in 5 mm. Hg vapour); and if we consider the curve beyond that value, it will be a simple exponential curve with the coefficient of extinction $\sqrt{\frac{1}{\tau D}}$.

If we measure, then, two values of N for two x -values in that region, we can calculate this coefficient. Now, judging from the absorption of 4046 for different distances x (see figs. 1 and 2, Pl. XXV.) and from the intensity distribution of the forbidden line 2356 along the slit (see fig. 3, Pl. XXVI.), we may make the rough estimate that N decreases to $\frac{1}{2}$ of its value from $x = 1.5$ to $x = 2.5$ cm. * when water vapour at 0.2 mm. pressure is in the tube. We therefore have

$$\sqrt{\frac{1}{\tau D}} = \ln 2 = 0.7 \quad \text{and} \quad \tau = \frac{2}{D}.$$

* An exact measurement has not yet been attempted, but could be easily done; the present is only a provisional calculation.

Now, the diffusion coefficient of excited Hg in H₂O is given by the kinetic theory as $D = \frac{118}{p}$, where p is the pressure in mm.

At a pressure $P = 0.2$ mm. we have

$$D = \frac{118}{0.2} = 590 \quad \text{and} \quad \tau_{P_0} = \frac{2}{590} = \frac{1}{295} \text{ sec.}$$

under our conditions. This value of the mean life of the metastable atoms is in good agreement with the results of Dorgelo (*l. c.*). The number of collisions of a $3P_0$ atom with water molecules at 0.2 mm. pressure is of the order of magnitude of $2 \cdot 10^6$ per sec., which means that a metastable atom can survive 10^4 collisions with a water molecule before giving up its energy in a collision of the second kind. Orthmann and Pringsheim* found a similar value for collisions with neutral mercury atoms at atmospheric pressure in presence of 0.01 mm. of thallium vapour.

— Discussion.

Several authors have attempted to measure or calculate the long lifetime of the metastable atoms postulated by Franck and Reiche† in order to describe the absorption of certain He lines observed by Paschen. M. Marshall‡, applying the method of the low-voltage arc with alternate current, used by Kamenstine§ for helium, which apparently gives a very direct method of measuring the life of the metastable atoms to the case of mercury, found rather surprising results. He finds that the higher metastable level 2^3P_2 has a longer life ($\frac{1}{24}$ sec.) than the lower one 2^3P_0 ($\frac{1}{70}$ sec.), and that the admission of gases like CO, CO₂, N₂, H₂O, and H₂ had no influence upon the life of 2^3P_2 , but shortened the life of the lower level 2^3P_0 and all the gases by the same amount. These results are in open contradiction with all subsequent experience. There is no doubt now that the life of the higher metastable level is shorter than that of the lower one, and that the first is very sensitive against collisions with any of the named gases, while the second can endure thousands of collisions with N₂, CO, or H₂O. C. Eckart|| showed that the results

* Orthmann & Pringsheim, *Zeit. f. Phys.* xxxv. p. 626 (1926).

† Franck & Reiche, *Zeits. f. Phys.* i. pp. 154, 320 (1920).

‡ Marshall, *Astrophys. Journ.* lx. p. 243 (1924).

§ Kamenstine, *Astrophys. Journ.* xlix. p. 135 (1924).

|| Eckart, *Phys. Rev.* xxvi. p. 454 (1925).

of Kamenstine and Marshall were probably due to the survival of ions rather than metastable atoms. Dorgelo* made a direct measurement of the life of the metastable atoms in neon and Hg, observing the absorption of the lines footing on the metastable levels a certain time after the electrical excitation of the vapour had ceased. He found that the life of the higher level (2^3P_2) was about $\frac{1}{200}$ sec. in pure mercury vapour at room temperature, and the life of the lower one (2^3P_0) still longer than this value, and that both were very sensitive to impurities, especially to the presence of hydrogen†.

The time calculated by us for the level 2^3P_2 (10^{-5} sec.) is considerably shorter than the result of Dorgelo, but we must remember that the experimental conditions are completely different. In the case of Dorgelo, the life of the metastable atoms is only shortened by collisions with impurities or with the walls of the tube, while in our case of very intense side illumination, the absorption of lines like 5461, 3650, and 4046, 2967 by the metastable atoms must shorten the lives of them in a sensible degree. Meissner and Graffunder‡ have recently found that in the case of neon the life is considerably reduced by side illumination.

In the case of 2^3P_0 , the lower level, the effect of side illumination is less noticeable because the total amount of metastable atoms in this level is enormously larger than in the case of the higher level.

On the whole, we can say that the life of the metastable atoms, when undisturbed by exterior agencies, is probably limited only by the emission probability of the "forbidden lines" 2270 and 2656, which for the last one has been measured by the author to be about 10^8 times smaller than for 2537§. Since the life of the resonance level is 10^{-7} sec., the life of 2^3P_0 would be $10^8 \cdot 10^{-7} = 10$ sec. under best conditions. These conditions may exist in some stars.

The Amount of Metastable Atoms.

Formulas (31) and (33) show that the density of metastable atoms will be governed by the constant π . Because in many physio-chemical investigations it is desired to have

* Dorgelo, *Physica*, v. p. 429 (1925).

† G. Ramsauer (*Naturwissenschaften*, xvi. p. 576 (1928)); and T. Asada, R. Ladenburg, and W. Tietze, *Phys. Zs.* xxix. pp. 549, 708 (1928) have recently published new measurements of τ_{P_0} obtaining a value of 10^{-3} sec. in agreement with my result.

‡ Meissner & Graffunder, *Ann. der Phys.* lxxxiv. p. 1041 (1927).

§ Details of the calculation will appear shortly.

a large concentration of metastable atoms, we may discuss it more in detail. At the same time, we can try to explain the fact that CO is very efficient at low pressures in producing metastable atoms, but not at pressures above 0.2 mm. Considering (29'), (30), and (32), we can write π in the following form:—

$$\pi = \frac{zE_1}{z^2E_1E_0 + z(E_1B_0 + E_0A_1) + A_1B_0} \cdot \cdot \cdot \quad (34)$$

If the efficiency of collisions of the second kind with the metastable atoms for the gas in consideration is very small ($E_0=0$), π will reduce to

$$\pi = \frac{zE_1}{B_0(zE_1 + A_1)}; \cdot \cdot \cdot \cdot \cdot \quad (34')$$

that means π will increase steadily with the pressure at a rate depending on the value of E_1 . For smaller E_1 (efficiency of collisions quenching 2^3P_1) we shall require a larger z (pressure) to obtain the same amount of metastable atoms, as in the formula only the product zE_1 appears, and not z or E_1

separated. The maximum of π will be $\pi_{\max.} = \frac{1}{B_0}$, and will be obtained for $z=\infty$. The number of metastable atoms would then be given (see formula (33), where $e^{-\gamma}$ is small and can be neglected) by

$$N_{P_0 \max.} = \frac{I_1^0}{B_0},$$

and could be still increased, diminishing the absorption probability of lines like 4046 ($B_0 = b I_{4046} + b' I_{2967} + \dots$ if b are the absorption coefficients), which can be done by absorbing them out of the arc light without absorbing 2537. One-half of the maximum value would be obtained already when $zE_1 = A_1$; that is, when the number of efficient collisions is equal to the probability of emission of 2537, which is the inverse of the mean lifetime of the level 2^3P_1 . Now, this life is known to be 10^{-7} sec., and Wood's measurements show that the line 5461 in fluorescence, which can be used as a measure for the number of metastable atoms N_{P_0} , as 3650 was used for N_{P_1} , increases to one-half of its maximum intensity at a nitrogen pressure of 0.65 mm. At this pressure the number of collisions z per sec. of excited atoms (diameter 1.62 times normal) with nitrogen molecules is $\cdot 7 \cdot 10^7$ per sec., which allows us to calculate E_1 , the efficiency of the quenching collisions of nitrogen, as

$$E_1 = \frac{A_1}{z} = \frac{10^7}{\cdot 7 \cdot 10^7} = 1.4.$$

This value is in contradiction with the value 0.013 calculated by Stuart. If we suppose with Foote* that $E_1=1$, that is, that every collision is effective with the 2^3P_1 level, we shall obtain a mean life $\tau_{P_1}=1.4 \cdot 10^{-7}$, which is something larger than the known value. We will consider this point and the quenching of resonance radiation by gases in detail in a subsequent paper.

In our practical case the collisions of the second kind will play always a certain rôle so that E_0 will never be completely $=0$; but it seems that gases like water vapour (avoiding free H_2 or O_2), argon, and, more or less, nitrogen behave very nearly ideally.

If E_0 cannot be neglected, but is still small, the number of metastable atoms will at first increase with the pressure and proportional to the efficiency E_1 of collisions with the level 2^3P_1 , as in the ideal case, but afterwards the term in z^2 (formula 34) will predominate and π will decrease again. The maximum will be obtained for

$$z = \left(\frac{A_1 B_0}{E_1^2 E_0} \right)^{\frac{1}{2}},$$

and will occur at lower pressures the larger the product $E_1^2 E_0$ is. This product seems to be larger in the case of CO than in the case of N_2 . The maximum concentration of metastable atoms is reached with CO at about 0.2 mm., and with nitrogen at from 5 mm. to 70 mm., depending on its purity. This explains the special behaviour of CO with increasing pressure, as shown by fig. 1 (Pl. XXV.).

The Absorption of 4046, and the Density of 2^3S_1 for Low Pressure.

The absorption of the line 4046 of the arc will be different for the case of low pressure when diffusion takes place, and for the case of higher pressures when it does not. In the first case the absorption law will be simply

$$I_{4046} = I_{4046}^0 e^{-\lambda x}, \quad . \quad . \quad . \quad . \quad (35)$$

where λ is proportional to \bar{N}_{P_0} : $\lambda = f \cdot \bar{N}_{P_0} = \mathfrak{A} \cdot I_1^0$. That absorption law is similar to the law for the resonance line 2537. The only difference lies in the numerical values of the absorption-coefficients. For low gas pressures the absorption of 4046 is considerably smaller than the absorption of 2537, due to which I_{4046} will be very nearly constant

* P. D. Foote, Phys. Rev. xxx. p. 288 (1927).

along the cross-section of the tube. Similar laws will govern the absorption of the lines 2967, 2753, 2534.

To calculate the number of atoms in 2^3S_1 we need only consider the absorption of 4046 and can neglect the atoms brought up by 4358, because when gases are present (large concentration of metastable atoms) the absorption of 4358 is many times smaller than the absorption of 4046.

The number of atoms that reach the level 2^3S_1 in the time unit will be then

$$-d(I_{4046}) \cdot dx = \lambda I_{4046} dx = S \cdot I_1^0 \cdot I_{4046} \cdot dx;$$

the number of atoms that leave it

$$N_s \cdot \frac{1}{\tau_s} dx,$$

where τ_s is not only determined by the emission probabilities of the lines originating in the level, as in the case of vacuo (see formula (21)), but also by the collisions of the second kind :

$$\frac{1}{\tau_s} = \epsilon_0 + \epsilon_1 + \epsilon_2 + D_s.$$

Therefore

$$N_s = \lambda \tau_s I_{4046} = S \cdot \tau_s \cdot I_1^0 \cdot I_{4046}^0 \cdot e^{-\lambda x}, \quad . \quad . \quad (36)$$

gives the density distribution of the excited atoms on the level 2^3S_1 . The intensity of the lines emitted by the excited atoms in that level will be

$$J_{4358} = \epsilon_1 \cdot N_s, \quad J_{4046} = \epsilon_0 N_s, \quad J_{5461} = \epsilon_2 N_s, \quad . \quad (37)$$

where the ϵ_1 , as in the case of vacuo, are the transition probabilities for each of the lines. We see that the intensity distribution along the cross-section of the tube is governed by the absorption of the line 4046, and must therefore be nearly constant. We shall see presently that this is confirmed by the experiment. The intensity curves of all the lines emitted by levels supplied with electrons mainly by absorption of the metastable atoms will be similar to those above. Such is the case for the levels 3^3S_1 , 3^3D_1 , and 4^3D_1 .

Case of Higher Pressure.

For the case of higher pressures of foreign gas, where diffusion does not occur, the absorption law of the line 4046 will be similar to the absorption law of the line 4358 in the case of vacuo (see formulas (16) and (17)), since the density

distribution of the metastable atoms in our case (formula (31)) is similar to the distribution in the level 2^3P_1 (see formula (12)) in the case of vacuo. It is then

$$I_{4046} = I_{4046}^0 e^{-\frac{\phi}{\gamma} I_1^0 (1 - e^{-\gamma x})} = I_{4046}^0 \cdot e^{-\frac{\phi}{\gamma} (I_1^0 - I_1)}. \quad (38)$$

The difference in the case of vacuo is that the constant ϕ is considerably larger than the constant α of 4358, due to the large number of atoms in the level 2^3P_0 . In the former case the exponential function was practically equal 1, while it is here a markedly falling curve, which is shown by the fact that the line 4046 of the arc is reduced to less than $\frac{1}{2}$ by the absorption in the cross-section of the tube (25 mm.), while the absorption of 4358 is not noticeable.

The level 2^3S_1 will be supplied, as before, practically only by the absorption of 4046. Its density distribution is then expressed by

$$N_s = \phi \cdot \tau_s \cdot I_1 \cdot I_{4046}. \quad . \quad . \quad . \quad (39)$$

The re-emission lines will be

$$J_{4046} = \epsilon_0 N_s, \quad \therefore J_{4358} = \epsilon_1 N_s, \quad \therefore J_{5461} = \epsilon_2 N_s;$$

or, if we write one of them in full, for instance, 4358,

$$J_{4358} = \epsilon_1 \cdot \phi \cdot \tau_s \cdot I_{2537}^0 \cdot I_{4046}^0 \cdot e^{-\gamma x} \cdot e^{-\frac{\phi}{\gamma} (I_{2537}^0 - I_{2537})}. \quad (40)$$

The Intensity Distribution of the Lines.

Now, let us compare this last expression with the corresponding ones for the cases of vacuo and at low pressures. In vacuo it was (see formulas (21), (20), (17), and (7), Theory I.):

$$\text{(vacuo)} \quad J_{4358} = \epsilon_1 \cdot \alpha \cdot \tau_s \cdot I_{2537}^0 I_{4358}^0 \cdot e^{-\gamma x} \cdot e^{-\frac{\alpha}{\gamma} (I_{2537}^0 - I_{2537})} *, \quad . \quad . \quad . \quad (41)$$

and in gases at low pressure ((37) and (36)):

$$\text{(low pressure)} \quad J_{4358} = \epsilon_1 \cdot \beta \cdot \tau_s \cdot I_{2537}^0 I_{4046}^0 e^{-\lambda x}. \quad . \quad . \quad (42)$$

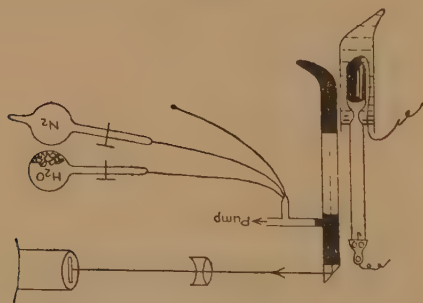
* A comparison of the two formulæ (40) and (41) allows us to calculate the ratio N_{P_0}/N_{P_1} of the amount of metastable atoms in the case of gases in regard to the amount of excited atoms in the level 2^3P_1 in the case of vacuo. We consider a volume element at the entrance-wall of the tube ($x=0$), and divide the two mentioned formulæ:

$$\frac{J_{4358}^0 \text{ (gas)}}{J_{4358}^0 \text{ (vacuo)}} = \frac{\phi I_{4046}^0}{\alpha I_{4358}^0}.$$

Now, this ratio has been found experimentally to be about 25 (enhancement of the lines by foreign gases). On the other hand, α is proportional

In the last case, as we have seen before, λ is very small, so that we should expect that the intensity distribution along the slit of the spectrograph, if we form an image of the cross-section of the tube upon it (see fig. 13), will be practically constant, or at least fall slowly. The central image of fig. 4 (Pl. XXVI.) shows this case. In the case of vacuo, the last factor is practically equal 1, as we have seen in the former paper, because of the faint absorption of 4358; thus the intensity distribution will be given by the absorption curve of 2537; that is, we should expect the intensity to fall exponentially along the slit with the extinction constant γ . The left-hand image of fig. 4 (Pl. XXVI.) gives 4358 for this case. Finally, in the case of gases at higher pressure, the last factor of formula (40) is no longer equal to

Fig. 13.



to the transition probability of 4358 and the density N_{P_1} (see formulæ (14) and (12)):

$$\alpha = \frac{A_{4358}}{I_1} N_{P_1}$$

and similarly

$$\phi = \frac{A_{4046}}{I_1} N_{P_0}.$$

Therefore

$$25 = \frac{A_{4046}}{A_{4358}} \cdot \frac{I_{4046}^0}{I_{4358}^0} \cdot \frac{N_{P_0}}{N_{P_1}}.$$

In the arc

$$\frac{I_{4358}}{I_{4046}} = 2,$$

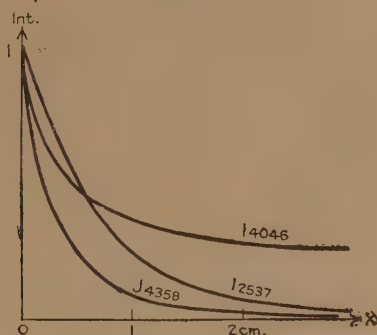
and therefore A_{4358}/A_{4046} is also = 2 (both lines are emitted by the same level, so that their intensity ratio gives at the same time the ratio of the transition probabilities), and we have that

$$N_{P_0}/N_{P_1} = 100.$$

This allows us to calculate the transition probability of the forbidden line 2656, as we shall see in a subsequent paper.

unity, but a falling function, and the intensity distribution of the line will be given by the product of two falling curves, the absorption curves of 2537 and 4046 of the arc. Fig. 14 illustrates this case. The lower curve is the product of the two upper ones, and represents the distribution of the intensity of 4358 we should expect in this case. The right-hand image of fig. 4 (Pl. XXVI.) gives 4358 while 2 mm. water vapour were present in the tube. We see that the results are completely in agreement with the theory. The slow falling of the intensity in the case of low pressure confirms once more the fact of the diffusion of the metastable atoms. The same changes are to be expected for all the lines emitted by levels supplied with electrons mainly from the level 2^3P_1 *in vacuo*, and from the level 2^3P_0 in presence

Fig. 14.



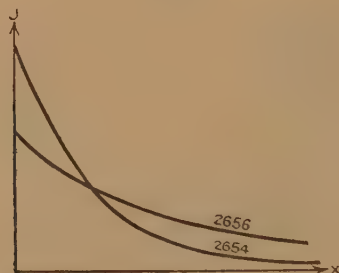
of gases (see fig. 2, Theory I., p. 1156), like 3^3S_1 , 3^3D_1 , 4^3D_1 . The line 2654 of fig. 3 (Pl. XXVI.) is included in this case. It is interesting to observe in fig. 3, *a* (Pl. XXVI.) that the forbidden line 2656 is stronger than the strongest line of the pseudo-triplet (2654) at the bottom of the slit*, but that the contrary happens at the top of it. Fig. 15 illustrates this case. This "crossing" of the intensities of the lines is due to the fact that the line 2656 requires only one absorption for its appearance, while 2654 requires two, and therefore behaves like 4358. We shall see in the following paper that the "crossing" of the lines is very useful in determining the origin of the band spectra that appear in the optically-excited mercury vapour under certain conditions. Special allowance must be made for the fluorescence lines 4046,

* See also R. W. Wood and E. Gaviola, *Phil. Mag.* vi. p. 271 (1928).

2967, 2753, and 2535, because they are partly re-absorbed in the tube before reaching the quartz prism at the top of it, due to the large concentration of metastable atoms. Fig. 6 (Pl. XXVI.) illustrates this case. We see that 4046, instead of increasing when water vapour is admitted into the tube, actually diminishes. This means that the absorption of it, proportional to the number of metastable atoms, increases faster than its intensity. This may be due to collisions of the second kind of atoms in the level 2^3S_1 .

Fig. 4 (Pl. XXVI.) shows, further, that 4358 increases about twenty times at the top of the slit if we introduce 2 mm. of water vapour in the tube, but does not change, or rather, decreases, at the bottom of it. This is specially plainly shown by fig. 5 of the same Plate. If we measure changes in the intensity of a line due to gases, the value obtained

Fig. 15.



will then greatly depend on the part of the image thrown upon the slit we allow to enter the spectrograph: then, it is usual to restrict the length of the slit in order to get more images into the plate. We can measure a *decrease* of 4358 due to H_2O or N_2 if we use the bottom of the line, while we obtain a 20 times increase using the top of it. Wood had already observed* that the increments due to 2 mm. nitrogen were in general larger for the region where the exciting beam enters than for the region of exit. That for 4046 he found the contrary is to be explained by re-absorption.

The Density Distribution in the Levels 2^3P_2 and 2^3P_1 .

We have already seen that the effect of gases is to decrease the number of atoms on the level 2^3P_2 as a result of collisions.

* Phil. Mag., Sept. 1927, p. 486.

of the second kind, and to increase it again if the pressure grows, because of the enormous enhancement of the green line which supplies that level with electrons. Because no diffusion of the atoms in 2^3P_2 takes place, the density curve along the cross-section of the tube will be determined by the density distribution of the green line 5461 in each case; that is, it will fall exponentially in the case of vacuo, it will be practically constant in the case of gases at low pressure, and it will fall sharply in the case of higher pressures. The same will also be true for the upper levels communicating only with 2^3P_2 , like 3^3D_3 and 4^3D_3 ; thus the lines 3650 and 3021 will present the same changes of relative intensity along the slit, under different conditions, as the line 4358; their absolute intensity will decrease at first and increase afterwards, while the intensity of 4358 increases steadily with the gas pressure. These predictions have all been confirmed experimentally. The distribution in the level 2^3P_1 will not be changed by the gases; only its mean life will diminish, due to collisions of the second kind, and with it the number of atoms on that level. The density distribution of the level 2^1S_0 (see fig. 2, Theory I., p. 1156) will be then always given by the absorption curve of the resonance line 2537. The intensity of the line 4077 emitted by that level will then decrease with gases without changing its intensity distribution. That has been found also experimentally to be the case.

The levels like 3^3D_2 , 4^3D_2 , 4^1D_2 , etc., which are supplied with electrons more or less from both levels 2^3P_2 and 2^3P_1 at the same time and in comparable quantities, will take a position more or less midway between the behaviour of 3650 and 4077. The lines emitted by those levels will, in general, decrease if gases are present. That is really the case for the lines 3125, 3654, 3024, 2652, 2655, 5770. Fig. 7 (Pl. XXVI.) shows the clear decrease of 3125 if gases are admitted; also that the decrease is stronger at the bottom than at the top of the line, as would be expected. The level 3^1D_2 occupies a special position in that it communicates already with the level 2^3P_0 by means of the line 2967.5, but this line is extremely weak; thus the density of the level decreases with gases, but less rapidly than the level 3^3D_2 . This explains the different behaviour of the yellow lines. The intensity of both lines decreases if gases are admitted, but 5770 about twice faster than 5790. The line 3131 takes a position midway between the behaviour of 4358 and 3125, due to the fact of its being a double line. The same is true of 3663 and 2967.

The special behaviour of the levels 3^3S_1 , and 3^1S_0 in the case when the tube is illuminated through a combined chlorine-bromine filter and gases are admitted (see R. W. Wood, *Phil. Mag.*, Sept. 1927, p. 480), has been satisfactorily explained by Beutler and Josephy* to be due to the fact that those levels have an energy very nearly equal to double the energy of a metastable atom; and it seems that, by collisions of two metastable atoms, there is a large probability for one of the atoms to take over the whole energy, provided the rest of the energy that has to be transformed in kinetic energy is small.

We see, then, that the behaviour of all the lines appearing in the mercury fluorescence can be readily explained by means of our theory.

Summary.

(a) The increases and decreases of the intensities of the mercury lines in the optical excitation of mercury vapour when foreign gases are admitted into the fluorescence tube are readily explained, using the results of our theory on the optical excitation of mercury vapour (Theory I.).

(b) The influence of diverse gases upon the absorption of the line 4046 by the metastable mercury atoms has been studied experimentally in order to determine the amount of metastable atoms produced by each of the gases at different pressures.

(c) Diffusion of metastable atoms has been directly demonstrated, showing their long lifetime.

(d) The higher metastable level 2^3P_2 is very sensitive to collisions with gas molecules, and its lifetime when no foreign gas is present has been calculated to be of the order 10^{-5} sec.

(e) The mean life of the lower metastable level 2^3P_0 has been calculated to be of the order of $\frac{1}{300}$ of a second under our conditions, and a further calculation shows that it can increase to about 10 seconds under ideal conditions (in stars, for instance).

(f) The efficiency of quenching collisions of nitrogen with excited atoms in the resonance level is found to be of the order of magnitude 1, as assumed by Foote, and not 0.13, as calculated by Stuart.

(g) The number of metastable atoms produced by the presence of a few millimetres of nitrogen or water vapour

* Beutler & Josephy, *Phil. Mag.* v. p. 222 (1928).

is estimated to be about one hundred times larger than the number of excited atoms in the resonance level.

(h) The different changes of the intensities of the lines along the slit of the spectrograph when gases are admitted and an image of the cross-section of the tube is formed upon it, are explained for every one of the lines appearing in fluorescence.

Professors R. W. Wood and K. F. Herzfeld had the kindness to read this work in manuscript, and to suggest many improvements, for which I wish to express my indebtedness to them.

The Johns Hopkins University,
Baltimore, Md.
June 30, 1928.

CXVI. *Photosensitized Band Fluorescence of OH, HgH, NH, H₂O, and NH₃ Molecules.* By E. GAVIOLA, Ph.D., Fellow of the Int. Educ. Board, and R. W. WOOD, LL.D., For. Memb. R.S.*

[Plates XXVII. & XXVIII.]

Introduction.

THE appearance of several band spectra as a result of photosensitized fluorescence was observed by Wood ⁽¹⁾ in his early work on the optical excitation of mercury vapour, and a summary description (page 781), and a few photographs of the bands have been already published. The OH band ("water-band") at 3064 was especially conspicuous, and appeared when nitrogen was present in the tube ⁽²⁾. During the work of the authors on the best conditions for the appearance of the "forbidden line" 2656 of mercury ⁽³⁾, it was observed that the OH band was present in the fluorescence also when water vapour is introduced into the tube, if care was taken that too much free hydrogen did not accumulate in the tube as a result of the decomposition of the water molecules into H and OH, which can be easily avoided by admitting a suitable quantity of oxygen, which takes care of the excess of free hydrogen by combining with it to form HO, H₂O, and H₂O₂. It was also observed that in general the conditions under which the forbidden line 2656 was brightest were the same for which the OH band appeared

* Communicated by the Authors.

with the maximum intensity, which is due to the fact that both are directly or indirectly originated by the presence of a large amount of metastable atoms with electrons on the level 2^3P_0 .

A more detailed study of the bands was taken up in the present work in order to identify the rest of the bands and to find out the conditions under which each of them appears, together with the possible chemical reactions that give rise to the molecules responsible for the emission of the bands. As an additional result very interesting data on the dissociation energy of water and nitrogen have been found.

Apparatus.

The apparatus was the same as described in the earlier papers (see fig. 13, Theory II., p. 1186). A drop of mercury was always at the bottom of the resonance tube. The desired gases could be admitted through capillaries connected with the different bulbs or the air of the room, and a palladium tube served for the admission of hydrogen, while the resonance tube was disconnected from the pump by a barometric mercury seal. The fluorescence tube was always saturated with mercury vapour and at room temperature.

Conditions for the Appearance of the Bands.

OH and HgH.—If the tube is evacuated and the mercury diffusion pump kept running no bands appear, with the exception of a faint one beginning at 2537 and fading rapidly towards the red side of the spectrum, in spite of fairly long exposures. If, now, 2 to 10 mm. of nitrogen are admitted, and if this nitrogen has not been specially freed from humidity, the OH band at 3064 and 2811 appears fairly bright, and further to the red a set of bands with clearly separated lines and with heads at 4222, 4012, 3724, 3509, etc., which can be obtained on the plate with a few minutes' exposure. The spectrum 1 of fig. 1 (Pl. XXVII.) shows this case, and was taken while 5 mm. of moist nitrogen were in the tube. A rough measurement of the set of bands at the red side of the OH band 3064 showed that they are identical with the mercury hydride bands, which were formerly erroneously classified as the "mercury band spectrum."

If we introduce a very small amount of oxygen (.001 mm.) into the tube containing the moist nitrogen, the mercury-hydride bands disappear as shown by spectrum 3 (fig. 1), leaving the OH bands stronger than before (not shown stronger in the photograph because 3 has a shorter exposure

than 1), and a diffuse band with maxima at 3360–70 Å. (indicated by an arrow in spectrum 3) which was rather faint in spectrum 1 increases considerably in its relative intensity.

NH.—This band has been found to be the so-called “ammonia” band, due probably to a NH molecule, which will be discussed more fully presently. If we admit more oxygen to the tube, the NH band at 3360–70 Å. disappears also, leaving the OH bands alone, as shown in spectrum 4. All these changes are perfectly reproducible, and, with a little practice, it is easy to obtain any of the desired band combinations

H₂O and HgH.—If we pump out the nitrogen and introduce 2 mm. of water vapour from a bulb containing CuSO₄ crystals, we obtain spectrum 2 of fig. 1 (Pl. XXVII.), which shows the OH and the HgH bands as in the case of nitrogen, but in which a new continuous spectrum appears extending from 2537 to 3200 Å. with a maximum around 2800 Å. very clearly visible in spectrum 2, forming a background for the OH band at 2811. The NH band of the former case is now absent, as was to be expected.

It is interesting to compare the HgH bands obtained with nitrogen and water vapour. We see in spectra 1 and 2 of fig. 1, or better in its enlargement in fig. 2 (Pl. XXVIII.), that in the case of water vapour the band-heads are much brighter than the higher rotational terms, while the contrary happens in the case of nitrogen. The very distinct band-head at 3722–28 Å. (fig. 2) in the case of water appears lost among the tail lines of the band 4012–17 in the case of nitrogen. This curious disparity might be due to the fact that water vapour quenches the higher rotational levels, throwing the excited HgH molecules to lower levels, an effect which would not be exerted by nitrogen.

If we introduce oxygen (few thousands of mm.) to the tube containing about 2 mm. water vapour, we obtain spectrum 5 of fig. 1. The HgH bands have disappeared, leaving the OH and the continuous band at 2800 Å. alone. The intensity of the continuous band at 2800 is proportional to the amount of water vapour, provided the little free hydrogen that develops is continually neutralized with oxygen.

NH₃.—We would confirm the results of Dickinson and Mitchell^{(14), (15)} that the introduction of NH₃ in the tube produces the 3360–70 band, and in addition to it a continuous band extending from 2900 to 4000 Å. with a maximum at about 3450 Å. Spectrum 6 of fig. 1 was taken while about 5 mm. of N₂ and a few tenths of a millimetre of NH₃ were in the tube, and shows well the continuous band and the

3360-70 band at the long wave-length side of the line 3341 of mercury. It is interesting to observe that the OH band at 3064 has disappeared for the first time, or is at least greatly reduced from its customary intensity, which is probably due to the formation of some $\text{NH}_3\text{—OH}$ or similar molecules, which take care of the OH formed, before it has a chance of being excited by an excited mercury atom.

Spectrum 7 shows the effect of a mixture of nitrogen, water vapour, ammonia, and some air for neutralizing the excess of hydrogen; all of the bands described so far appear together, demonstrating the possibility of the coexistence of N_2 , H_2O , OH, NH, NH_3 , and HgH molecules.

The Intensity Relations.

In a previous paper the authors have described ⁽⁴⁾ how the intensity of the different mercury lines in fluorescence is proportional to the first, second, or third power of the intensity of the exciting light, according to the number of successive absorptions necessary for the emission of each line, and how this could be easily tested by reducing the primary intensity a known number of times, using a wire gauze interposed between the arc and fluorescence tube and measuring the consequent reduction in the intensity of each of the secondary lines. If the primary light is reduced 5 times, the resonance line 2537 and the "forbidden line" 2656 are decreased 5 times, nearly all of the others 25 times (or 5^2), and 3650 and 3021 125 times ($=5^3$). Knowing this we can tell, independent of any level diagram, that 3650 requires three successive absorptions for its emission, while 2656 requires only one. The theoretical foundation of this rule has been given in a paper by one of us (Theory I.). Now, we can apply the same test to the bands, and that will help us to guess the chemical gas-reactions which go on in the tube and give rise to the bands. All of the bands are produced by collisions with excited mercury atoms, and not by direct absorption of light of the mercury arc, which is plainly proved by the fact that, as soon as the line 2537 of the arc reverses owing to overheating of the arc or to absence of the deflecting magnetic field, the bands disappear without exception, together with the mercury fluorescence. The power-relation of the intensity of a band in regard to the primary intensity tells us then how many excited mercury atoms are used in the production of an excited molecule responsible for the emission of the band.

As a result of careful measurements it has been found that the intensity of the two continuous bands due to the presence

of water vapour and ammonia are directly proportional to the primary intensity; the emission of them requires, then, a single collision with an excited mercury atom while the HgH band grows with the second power, which indicates that the emission of each light-quantum of the band requires the co-operation of two excited Hg atoms. The NH and OH bands appear to be proportional to a power intermediate between 1 and 2, the reason for which is to be sought in the greater stability of those molecules, some of which can survive, under given conditions, more than one excitation, a case which will be more fully discussed presently.

Fig. 4 (Pl. XXVIII.) gives an illustration of the wire-gauze method: spectrum *a* was taken while nitrogen, ammonia, and some water and air were in the tube, and shows the 3064 OH, the continuous ammonia band, the 3360-70 NH, and the 4012 HgH band; spectrum *b* was taken with exactly the same mixture while a wire gauze reducing the primary intensity about 4 times was interposed between arc and tube and the time of exposure increased about six-fold: bands proportional to the first power should be enhanced 1.5 times, while those proportional to the second should diminish about ten-fold in image *b*. We see that the continuous NH₃ band has become enhanced, while the HgH band-head at 4012 has practically disappeared and the NH and OH bands are greatly reduced in intensity. Removing the gauze and giving a short exposure again, we obtained an image equal to *a*, showing that the gas mixture had not changed practically during the experiment. It is curious and interesting that the intensities of different bands appearing as photosensitized fluorescence can be changed relative to each other simply by modifying the intensity of the exciting light.

There is another very elegant and simple method of determining the power relation of the intensities: the falling off of the brightness of the bands along the cross-section of the tube. If we form an image of the cross-section of the tube upon the slit of the spectrograph, we obtain a spectrum like the one in fig. 3 (Pl. XXVIII.), which shows that the bands decrease in their intensity along the slit with different rates of speed. This rate will depend on the way the bands are excited by the excited mercury atoms.

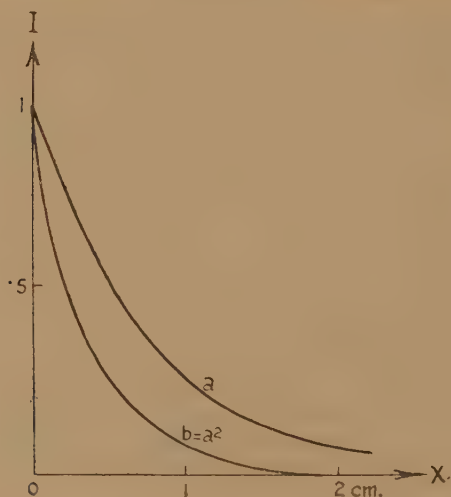
The only excited atoms which come into consideration for the excitation of the bands are the atoms in the resonance level 2^3P_1 and the metastable ones in the lower level 2^3P_0 . All other excited atoms are so few in number and of such short life that they have little or no chance of hitting any

molecules if the gas pressure is kept below a few millimetres, as has always been the case in the present work. Now the density distribution of the relevant atoms along the cross-section of the tube is given by the absorption law of the line 2537 of the arc

$$I = I^0 e^{-\gamma x},$$

which represents an exponential falling curve (see E. Gaviola, Theory II., p. 1187) like curve *a* in fig. 5. The intensity distribution of the bands, whose intensity is directly proportional to the primary intensity, that is, to the number of excited atoms, will be given also by curve *a*, while the bands propor-

Fig. 5.



tional to the second power will decrease along the slit with the square of curve *a*, which is represented by curve *b* in fig. 5. (A similar condition occurred in the case of the "forbidden line" 2656 (first power) as compared with 2654 (second power), and was illustrated by fig. 3, *a*, of Pl. XXVI. in Theory II.) We come now to fig. 3 (Pl. XXVIII.), which was obtained while 2 mm. of water vapour were present in the tube, and shows how the HgH bands decrease very rapidly in their intensity along the slit (quadratic relation), while the OH band does it less suddenly and the continuous H₂O band at 2800 less still (first power). That the OH band falls more rapidly than the continuous water band can be seen plainly by comparing this last with the 2811 branch

of the first, which is superposed on the continuous water band: the lines of the OH band appear bright upon the continuous background at the top of the slit, while they become lost in it at the bottom of the slit. Image 3 of fig. 1, which was taken in the same way, shows that the NH band at 3360-70 decreases along the slit parallel with the OH band. All of this confirms the results obtained with the wire gauge, that the intensity of both continuous bands is proportional to the first power, the HgH to the second, and the NH and OH bands to a power between the first and second.

Interpretation of Results.

Now that we know the conditions under which each of the bands appears and the number of excited Hg atoms which each molecule requires for its production and excitation, we can try to interpret the processes which take place in the tube in the different cases.

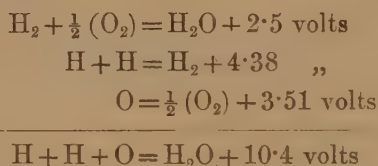
The Action of Water Vapour.

Let us consider first what happens when we introduce a few millimetres of water vapour into the tube containing excited mercury vapour; Wood⁽¹⁾ and, later, Senftleben & Rehren⁽¹⁷⁾ and Bates⁽¹⁸⁾ have observed that the H₂O molecule is dissociated in this case, and they were able to detect the presence of free hydrogen after the illumination. The appearance of the HgH and OH bands in our case confirms that dissociation takes place, and the fact that a little oxygen is able to bring the radiation back to full intensity when it begins to decrease by continued operation of the tube, shows the presence of free hydrogen which quenches the fluorescence. So far our results are in full agreement with those of the previous authors. Senftleben and Rehren concluded that the dissociation energy of H₂O into H and OH had to be smaller than 4.9 volts, the excitation energy of the mercury atoms. They showed also that only the reaction

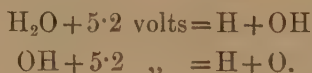


comes into consideration. Now, on the other hand, it has been found by us that water vapour is most efficient in producing metastable Hg atoms, which shows that by collisions of an H₂O molecule with an excited Hg atom in the 2³P₁ level in most cases no dissociation takes place, but that the atoms are thrown down to the metastable level 2³P₀,

as happens with N_2 . Furthermore, we have seen in our calculation of the lifetime of metastable atoms (Theory II.) that these atoms can survive at least 10^4 collisions with water molecules without giving up their energy. These facts speak in favour of the assumption that 4.9 volts are probably not quite sufficient for the dissociation of H_2O into H and OH, and that dissociation takes place only in the very few cases when the difference of energy can be taken out of the kinetic energy of fast-moving molecules. This is corroborated by the fact that Senftleben could never obtain more than 10^{-4} mm. of H_2 out of 4.6 mm. of water vapour after one illumination, and that Bates found for the reaction a very low efficiency compared with other processes. The dissociation energy of H_2O into $H+H+O$ is 10.4 volts; therefore



If we assume with Senftleben and Rehren that the dissociation into H and OH requires less than 4.9 volts, we shall have to admit that OH requires more than $10.4 - 4.9 = 5.5$ volts to dissociate. There is no good reason why the separation of the first H atom from $H-O-H$ should require at least 0.6 volt less energy than the separation of the second one. We have seen that our results make it probable that the dissociation energy of H_2O into H and OH is slightly more than 4.9 volts. If we assume that the separation of each of the H atoms from H_2O requires about the same energy, we obtain 5.2 volts as the linkage energy of $H-OH$ and of $O-H$:—



These two values need not, of course, be absolutely equal. All that our results say is that the value for the first reaction is slightly larger than 4.9 volts. The value 5.2 volts is quite plausible if we consider that at room temperature about $\frac{1}{2} 10^{-5}$ of the molecules have a kinetic energy sufficient to make up the difference between the 4.9 volts of the excited mercury and the required 5.2 volts. This proportion represents about the number of collisions effective in dissociating H_2O . Water vapour is practically inoperative in destroying

the metastable atoms in the level 2^3P_0 , because in this case the difference between the 5.2 volts required and the 4.68 volts of the mentioned atoms is too large to be taken out of the heat energy of the vapour.

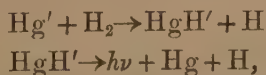
Resuming, we can say that the action of water vapour consists mainly in the bringing of excited atoms, which were in the level 2^3P_1 , down to the metastable level 2^3P_0 as a result of collisions, very few of which may lead to dissociation of H_2O into H and OH, and that collisions with metastable atoms are completely ineffective.

The HgH Bands.

The mercury-hydride bands have been carefully measured by Liese⁽⁵⁾, and afterwards by Hulthén⁽⁶⁾, who attributed them to a HgN molecule. Kratzer⁽⁷⁾ objected that the momentum of inertia of HgN would be too large for the bands and suggested that they may be due to mercury hydride instead—a suggestion that was accepted by Hulthén⁽⁸⁾ and supported by Mulliken⁽⁹⁾. Compton and Turner⁽¹⁰⁾ found that the bands appear in electrical discharge-tubes only when mixtures of mercury and hydrogen are present, and assumed that the reaction involved was



They tried to excite the HgH bands optically with a mercury arc, but without success, which was probably due to the fact that they had too much free H_2 in the tube which destroyed the excited mercury atoms, so that, also supposing that HgH were formed according to the reaction given above, the HgH molecules would have no chance of being excited by collisions with further excited Hg atoms, which is necessary for the emission of the bands. We shall see later that the reaction involved is probably $Hg' + H_2 \rightarrow Hg + 2H$, and not the one given above. In a further analysis of the bands, Hulthén⁽¹¹⁾⁽¹²⁾ calculated the dissociation energy of the normal HgH molecule to be 0.37 volt, and assumed that the reaction involved⁽¹²⁾ was

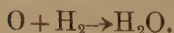


where the excited Hg atom was supposed to be in one of the 2^3P levels. This reaction is not possible because the energy of the excited Hg in the levels 2^3P is not nearly sufficient to dissociate the hydrogen molecule (4.4 volts) and at the same time excite the HgH molecule, for which at least

4 volts are necessary. The second assumption that the excited mercury-hydride molecule dissociates after emission is in agreement with our results, as we shall see later.

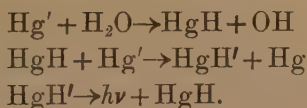
We have seen above that the HgH bands appear when water vapour, or also when moist nitrogen, is present in the tube. Both gases are very effective in producing a large concentration of metastable atoms, and in both cases a small amount of free hydrogen is developed in the tube. These are the two necessary conditions for the appearance of the HgH band. In fact, if we introduce pure dry nitrogen, metastable atoms are generated, but the band does not appear. Introducing, now, a small amount of hydrogen (0.001 mm.) through the palladium tube, the band shines out immediately. On the other hand, a small amount of hydrogen alone is not able to produce the HgH band, in spite of the presence of excited mercury vapour, showing that the presence of a large concentration of metastable atoms (generated by the nitrogen) is necessary. This discards the assumption of Hulthén⁽¹²⁾ that collision of an excited mercury atom with hydrogen would produce an *excited* HgH' molecule and a H atom, for in this case the band should appear with hydrogen alone, but we have seen already that this reaction is also impossible from the energy point of view. If the amount of hydrogen introduced through the palladium tube is increased, the HgH band fades away together with the whole fluorescence, owing to the quenching action of hydrogen.

We have also seen above that the admission of a little oxygen (or air) produces the disappearance of the HgH band and at the same time enhances the OH band. Obviously, the oxygen neutralizes the little free hydrogen forming more OH, and at the same time the concentration of metastable atoms increases, due to the disappearance of the quenching free hydrogen. The reaction involved is probably

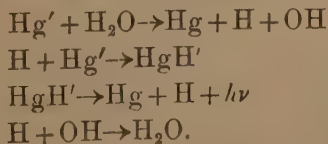


When about 2 mm. of nitrogen are present in the tube, the disappearance of the HgH band is then due to the full neutralization by the oxygen of the little free hydrogen present, giving OH and H₂O as a result, and since no free hydrogen is left, no HgH can be formed. When 2 mm. of

water vapour are present in the tube, the disappearance of the HgH band produced by a little oxygen is not so easy to explain: Hulthén^{(11), (12)} has calculated that the linkage energy of normal HgH is 0·37 volt. This being so, the reaction $\text{Hg}' + \text{H}_2\text{O} \rightarrow \text{HgH} + \text{OH}$ is energetically quite possible if we admit for the dissociation energy of $\text{H}-\text{OH}$ about 5·2 volt, as we have done before. Now, if this reaction should occur to any considerable extent, water vapour would quench the resonance radiation without producing metastable atoms, and the energy would thus be used for the dissociation of H_2O into H and OH , and water would behave like hydrogen; but we know that this is not the case, and that by collisions with water the 2^3P_1 atoms fall down to the 2^3P_0 level, which shows that the above reaction occurs rarely, if at all. This fact could be interpreted either by assuming that the dissociation energy of $\text{H}-\text{OH}$ is more than $4\cdot9 + 0\cdot37 = 5\cdot27$ volts, or that HgH is not able to exist in the normal state, but only when it is excited. It is known⁽¹²⁾ that the excited molecule is more stable than the unexcited, and that excited ones probably dissociate after the emission of light. Furthermore, if normal HgH molecules were formed directly by collisions with water, and persisted for at least 10^{-3} sec., such molecules would have a good chance of meeting excited (metastable) mercury atoms, becoming excited by them, and emitting the HgH bands. The reaction would be



If this were the case, the emission of the HgH band in the case of water vapour should not depend on the presence of free H_2 ; on the contrary, it should be strongest when no quenching H_2 is present. We have seen that this is not the case: the HgH band disappears together with the free H_2 . Normal HgH is then not formed, or, if formed, it lives less than 10^{-3} sec. (time necessary to meet an excited atom) and dissociates. To describe the appearance of the HgH bands with an intensity proportional to the square of the arc-intensity, we propose the following reaction:—

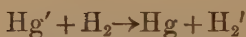


The concentration of H-atoms will be (in first approximation) in this case proportional to the exciting light-intensity; the concentration of Hg' atoms is also proportional to it. Thus the concentration of HgH' molecules and the intensity of the band emitted by them, which is proportional to the product of the two factors, should be proportional to the square of the primary light-intensity; and this is really the case, as we saw before*.

The appearance of the HgH band when N_2 and little H_2 are present in the tube can be described in the following way:—



or also



where H_2 in the second case would have to be brought up to some metastable state, in order to await the next collision with an excited mercury atom. This last reaction has already been suggested by Dickinson⁽²⁰⁾ and Mitchell⁽¹⁹⁾, in order to describe the photochemic formation of water out of H_2 and O_2 in the presence of mercury vapour. In both cases the quadratic intensity relation is satisfied.

The OH Bands.

The OH bands were discovered by Huggins and Liveing & Dewar⁽²¹⁾ in 1880, and studied and analysed afterwards by Watson⁽²²⁾, Tanaka⁽²³⁾, and Jack⁽²⁴⁾, among others. They often appear in discharge-tubes as an impurity.

In our case, as said before, the relation of the intensity of the band in regard to the primary intensity lies between the first and the second power, and we will try to interpret this behaviour. Let us consider the case when water vapour is in the tube. OH will be formed by following reaction:



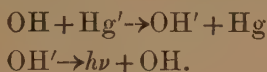
and the rate of formation, which we know is very small, would be proportional to the arc intensity (number of Hg'

* Another possible description of the facts is



where water would be brought up to some metastable level in order to await the next collision with Hg' .

atoms). The OH is a rather stable molecule, and by collision with another excited mercury atom will itself become excited and emit as a result of it the OH band :



If the lifetime of the OH molecule is such that it does not survive in general more than one excitation, the intensity of the band should be proportional to the second power of the arc intensity because each band-quantum would require two excited mercury atoms for its emission : one for the formation of OH out of H_2O and one for its excitation according to the reactions outlined above ; on the other hand, if the lifetime of OH is so long that it survives several successive excitations, the concentration of OH in the tube will be practically constant, and the chance of meeting an excited mercury atom will be simply proportional to the number of them ; that is, to the first power of the primary intensity. The experimental fact that the power relation lies between 1 and 2 shows that OH survives more than one excitation, but less than, say, three. The mean life of the OH molecule is then of the order of magnitude of the time-interval between two collisions with excited mercury atoms, which can be roughly calculated using the results obtained by one of us in Theory II. It was found there that we have in our own case about 100 times more metastable than $^3\text{P}_1$ atoms. Now, our resonance tube absorbs roughly 10^{18} 2537 light-quanta per sec. in a volume of 20 cm.³, and since the life of $^3\text{P}_1$ is 10^{-7} sec.,

$$\text{N}_{\text{P}_1} = 10^{18} \cdot 10^{-7} = 10^{11} \quad \text{and} \quad \text{N}_{\text{P}_0} = 100 \cdot 10^{11} = 10^{13},$$

which is about one hundredth of the number of normal atoms.

The number of collisions of a OH molecule with this number of metastable atoms is about 100 per sec., and the time between two consecutive collisions $\frac{1}{100}$ sec., which is then the order of magnitude of the lifetime of the OH molecule. Since the lifetime of OH is limited, it must be destroyed in some way.

Senftleben and Rehren⁽¹⁷⁾ assume that the reaction



might account for it, although they could not detect the formation of hydrogen peroxide. Marshall and, later, Bates & Taylor⁽¹⁸⁾ and Bonhoeffer & Loch⁽²⁵⁾ have detected and measured it. If we assume that this is the way in which

OH is destroyed, the probability of meeting another OH molecule must be of the same order of magnitude as the probability of meeting another excited mercury atom, which amounts to saying that the concentration of OH must be about equal to the concentration of excited mercury atoms. We know this last concentration to be

$$N_{P_0} = 10^{13} \text{ atoms.}$$

Now, knowing the concentration N and the mean lifetime τ , we can calculate the rate F of formation of OH since

$$F = N/\tau.$$

There are, then, $F = 100 \cdot 10^{13} = 10^{15}$ OH molecules produced per second.

The number of collisions of one 2^3P_1 atom with water molecules (water pressure 2 mm.) is of the order of magnitude of $2 \cdot 10^7$. The total number of such collisions is then $2 \cdot 10^7 \cdot 10^{11} = 2 \cdot 10^{18}$ per sec.; and since the number F of water molecules dissociated is 10^{15} , only one in $2 \cdot 10^3$ collisions leads to dissociation. This number is larger than the number found before for the ratio of molecules having a kinetic energy of 0.3 volt (difference between the 4.9 of Hg' and the assumed dissociation energy of 5.2 volts for the H_2O molecule). The agreement would be complete if we assumed 5.1 volts for the said dissociation energy, but we do not lay stress upon this calculation because the number of light-quanta emitted by the arc is not known with sufficient accuracy.

The NH Band.

The NH band at $3360\text{--}70 \text{ \AA.}$ was first photographed by Eder in 1892, who called it the "ultra-violet ammonia band," and obtained it by burning an ammonia oxygen flame. Deslandres calls it the third positive group of nitrogen, and Kaiser (v. p. 836) says that it doubtless belongs, not to NH_3 , but probably to NO. Later, Lewis⁽²⁶⁾ found that it appears in a discharge-tube with all mixtures of N_2 and H_2 , but not with N_2 or H_2 alone, and concluded that it "might reasonably be attributed to ammonia." Fowler and Gregory⁽²⁷⁾ published beautiful photographs of it. Bair⁽²⁸⁾ thought that the $3360\text{--}70 \text{ \AA.}$ band was very probably due to ammonia, and that "it may be due to a compound of nitrogen and hydrogen, which is more stable than ammonia." Barrat⁽²⁹⁾ was the first to suggest NH as the origin of the band, in spite of which Kwei⁽³⁰⁾ still believed it to belong to NH_3 . Finally,

Hulthén and Nakamura ⁽³¹⁾ analysed the spectrum and decided that it belonged to NH, which is in complete agreement with our results.

As we saw at the beginning, the NH band, together with the HgH and the OH band, appears if moist nitrogen is introduced into the tube. Apparently, the necessary factors for its production are, besides excited mercury atoms, nitrogen and very little free hydrogen; then, after a certain time of illumination, the 3360-70 band decreases in favour of the mercury hydride band, due probably to the fact that too much free hydrogen is developed from the moisture in the tube, which is confirmed by the fact that the introduction of a little oxygen restores the NH, diminishing at the same time the HgH band. The interesting fact that of the two hydride bands, NH and HgH, the nitrogen one reaches its maximum intensity in our case with a smaller hydrogen quantity than the mercury one, is confirmed by the following direct experiment: we admit to the tube only fully-dried nitrogen at a pressure of about 4 mm., and no bands appear; we warm the palladium tube with the reducing zone of a small gas flame in order to let hydrogen in at a very low rate, and we observe that the NH band appears first alone, reaches its maximum intensity and begins to decrease slowly when the HgH band first appears, increasing until it reaches a maximum, when the NH band has already weakened considerably. This curious difference in the behaviour of the two hydrides may be due to the greater stability of the NH molecule when very little hydrogen is present: in fact, if very little hydrogen is in the tube, it will be probably completely dissociated by collisions with excited mercury atoms, so that only hydrogen atoms will be present, which, if they meet a nitrogen atom, will be bound by it to form NH, and they remain bound to it for a long time, due to the great stability of this molecule. On the other hand, if they meet excited mercury atoms, they will form HgH, which will dissociate after emission of one quantum of radiation, leaving the H-atoms free for combination with nitrogen atoms, the result of which will be that in a short time all the hydrogen will be used up in the formation of NH, and that only this band, excited by collisions with metastable mercury atoms, will be present. If more hydrogen is admitted, H-atoms will be available for the formation of HgH and the emission of its band, which explains its enhancement, while, on the other hand, some of the NH will be destroyed by H₂ forming ammonia ($\text{NH} + \text{H}_2 \rightarrow \text{NH}_3$) or also by H forming NH₂, and at the same time the amount of metastable atoms will begin to

be quenched by the molecular hydrogen, which explains the decrease of the NH band. The destruction of NH to form NH_3 is supported by the fact that Noyes⁽³²⁾ found ammonia formed photochemically out of nitrogen and hydrogen under conditions similar to ours.

If the given explanation is correct, the intensity of the NH band in the case of very little hydrogen (NH appears alone) should be very nearly proportional to the first power of the arc intensity, for in this case the amount of NH present would be constant (great stability), and, excited again and again by collisions, the intensity of the band should be simply proportional to the number of collisions with excited mercury atoms; that is, proportional to the number of excited Hg atoms, or, what is the same, to the primary intensity. In the case of more hydrogen, which would put a limit to the life of the NH molecules, the concentration of the latter would depend on the arc intensity, and we should expect a higher power relation than the first. Now, this is precisely what happens: with very little hydrogen the intensity relation approximates to the first power, while with more hydrogen it approaches the second power. We have now to find an explanation for the appearance of the band with that intensity relation of the last case. NH is probably formed by the combination of atomic nitrogen and atomic hydrogen



giving an excited hydride molecule due to the heat of combination of about 4 volts (see Bates and Andrews⁽³³⁾). The number of excited molecules formed in this way is proportional to the product of concentrations of N and H, and since the concentration of atomic hydrogen is probably constant (due to the fact that all H_2 present is dissociated), the concentration of atomic nitrogen as a function of the primary intensity will determine the power relation of the intensities, which, as we know, lies between 1st and 2nd. Now, if we make an allowance for the NH molecules which are excited more than once during their lifetime, as was done in the case of OII, which lowers the power relation, we can assume that the concentration of atomic nitrogen is proportional to the square of the number of excited mercury atoms, which means that the production of a nitrogen atom requires two excited mercury atoms. This would be the case if we assume that N_2 is dissociated by a three-body collision with two excited mercury atoms



The only excited atoms which come into consideration are the 2^3P_1 with 4.9 and the metastable with 4.68 volts energy. The maximum energy available in the most favourable case for the dissociation of N_2 would be then 9.8 volts; two metastable atoms would give only 9.36 volts, which is 1.5 to 2 volts less than the value of 11.4 volts calculated by Sponer and Birge. We could secure more energy for the dissociation of N_2 if we suppose that mercury nitride is formed by the reaction



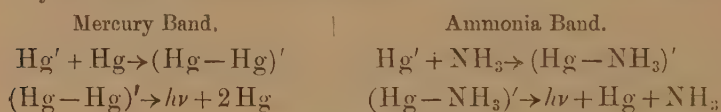
in which case the combination energy of HgN could be added; but we should then expect an explosive black deposit of mercury nitride which has never been observed in the tube in spite of operating it uninterruptedly for several days. Mercury nitride is not formed, and we have only 9.8 volts for the dissociation of N_2 . This would indicate that the dissociation energy of nitrogen is less than or about 9.8 volts, the value which recent results of several authors seem to show. To avoid the assumption of the low dissociation energy for N_2 we should be compelled to make hypotheses less plausible than this one*.

The Continuous Spectra.

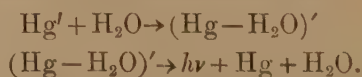
Two continuous spectra have been observed to appear as a result of photosensitized fluorescence as described above: the first one (when water vapour at pressures from 0.5 to 10 mm. is in the tube), at 2800 Å. (see spectra 2 and 5, figs. 1 & 3, Pls. XXVII. & XXVIII.), seems to have been first observed and photographed by Wood⁽¹⁾; the second one (when ammonia is in the tube), at 3400 Å., has been observed by Mitchell⁽¹⁵⁾ and perhaps before by Dickinson and Mitchell⁽¹⁴⁾, although it is not clearly stated in their paper: they speak of a "diffuse band with a maximum around 3370," which may also be the NH band at 3360–70 Å. The continuous band with a maximum at about 3400 Å. looks very similar to the ultra-violet band of mercury obtained by illuminating pure mercury vapour at 300° with a cadmium or aluminum spark, studied by Wood and Van der Lingen⁽³⁴⁾, Lord Rayleigh⁽³⁵⁾, Houtermans⁽³⁶⁾, Niewodniczanski⁽³⁷⁾, Pringsheim and Terenin⁽³⁸⁾, and others; and Mitchell

* The results of this investigation, specially in regard to the low dissociation energy of nitrogen, were already reported at the Washington meeting of the Am. Phys. Soc. in April 20–21, 1928. A part of them appeared in 'Nature,' Sept. 1st, 1928.

suggested that the band observed with mercury at 300° might be due to NH_3 contained as impurity, which is improbable since this band has been observed by all of the mentioned authors with equal intensity, and they very probably used mercury of different degrees of purity. The coincidence is probably more or less a chance due to the similar type of emission of both bands: the emission of the pure mercury band at 3400 is due, according to Houtermans and Niewodniczanski, to the dissociation of a quasi-stable molecule formed by collision of a metastable mercury atom in the level 2^3P_0 with a normal one, during which dissociation part of the energy of the excited atom is emitted and the rest transformed into kinetic energy of the separating atoms; on the other hand, the emission of the continuous NH_3 band is probably due to the dissociation of a quasi-stable mercury-ammonia molecule formed by collision of a metastable atom with a normal NH_3 molecule, dissociation occurring in the same way as in the former case.



The emission of the continuous water band at 2800 may be accounted for in the same way, only in this case the excited mercury atom which forms the quasi-stable molecule is surely a 2^3P_1 atom, since the band extends beyond 2656, as can be seen in spectrum 2, fig. 1 (Pl. XXVII.), which means that its emission requires more energy than that of a metastable atom. The reaction would be



The reactions outlined above are in agreement with the fact that the intensity of both the continuous bands is proportional to the first power of the primary light.

Summary.

(a) The photosensitized fluorescence of HgH , OH , NH_3 , $\text{Hg} - \text{H}_2\text{O}$, and $\text{Hg} - \text{HN}_3$ molecules has been observed, the conditions for the appearance of each of the bands determined, and the most probable chemical processes which give rise to them suggested.

(b) The dissociation energy of a water molecule into H and OH is probably about 5.2 volts, and not less than 4.9 as assumed by Senftleben and Rehren.

(c) The concentration of OH and of NH in the fluorescence tube is, under the best conditions, of the order of magnitude of the concentration of excited mercury atoms (10^{-5} mm. pressure).

(d) The dissociation energy of the nitrogen molecule seems to be less, or about, 9.8 volts, and not 11.4 as calculated by Sponer and Birge.

(e) Collisions of excited mercury atoms in the resonance level 2^3P_1 with normal water-vapour molecules may lead to several different processes: in most of the cases the excited mercury atom is thrown down to the metastable 2^3P_0 level, in a few cases (about 1 in 10,000 collisions) the water molecule is dissociated into H and OH, and finally in some cases (less than 1 in 1000) a complex quasi-molecule $Hg-H_2O$ is formed which dissociates, emitting the continuous band at 2800 Å.

(f) Collisions of excited mercury atoms in the resonance level with nitrogen molecules bring the first ones down to the metastable level; three-body collisions of two excited atoms with a nitrogen molecule may lead to dissociation of the nitrogen molecule.

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Johns Hopkins University.
July 28, 1928.

Addition by the correction.—It has been suggested by several authors that the activation of foreign gas molecules takes place mainly at the walls of the tube. We have not found any signs of it. The formation and excitation of all the bands observed by us is a gas reaction and the walls do not act as a catalyser.

CXVII. *Reversals in the Arc-Spectrum of Nickel.* By
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Low Terms in the Ni I Spectrum.

ACCORDING to Hund † the low terms in the spectrum of Ni I should be as in the following table, where the first two columns give the electron-grouping in the outer levels and the term-types of Ni II, the third and fourth columns give the resulting groupings and term-types for Ni I, and the last column the terms found in the spectrum by Bechert and Sommer ‡, with their values for the lowest component of each multiplet.

From this it will be seen that the lowest term so far observed is the 3F_4 term, which Bechert and Sommer have accordingly made the zero of their term-scheme.

Other atoms which might be expected to have a similar structure in their spectra are Pd I, Pt I, Cu II, Ag II, and

* Communicated by the Author.

† '*Linienpektren*,' p. 165 (Julius Springer, Berlin, 1927).

‡ *Ann. d. Physik*, lxxvii. p. 351 (1925).

Au II. The first, third, and fourth of these have been shown to have 1S_0 as the ground-term, while Pt I has 3D_3 , and Au II has not been analysed (according to the author's unfinished analysis it seems likely that it will not be 1S_0 , but probably a 3D term). It is accordingly not possible to conclude from similarity what the ground-term should be. The atomic-ray experiments of Gerlach would, however, suggest that the ground-term should be 1S_0 . This could be the 1S_0 term belonging to d^{10} predicted by Hund, and the \bar{S}_0^1 term of Bechert and Sommer would then have to be attributed to s^2d^8 .

TABLE I.

Ni I.		Ni II.		Terms observed.
Electron- grouping.	Term- type.	Electron- grouping.	Term- type.	
$s d^8$	4F	s^2d^8	3F	$f_4^1 = 0$
		$s d^9$	3D	$\bar{d}_3^1 = 204\cdot82$
	4P	s^2d^8	3P	$p_2^1 = 15609\ 81$
		$s d^9$	1D	$\bar{D}_2^1 = 3409\cdot95$
s^2d^7	2F	s^2d^8	1G	—
			1D	$\bar{D}_2^2 = 13521\cdot29$
d^9	2D	d^{10}	1S	$\bar{S}_0^1 = 14728\cdot92$

Under these circumstances it seemed worth while to explore the spectrum of nickel as far as possible towards the short waves, in an endeavour to find lines belonging to a hypothetical 1S_0 term. It would show its presence by very strong lines, easily reversible, with successive wave-number differences equal to the differences between the middle terms of Bechert and Sommer having $j = 1$. The region between 3858 and 2253 Å. U. has been covered by Majumdar* working with the oven and the under-water spark in the search for low terms, so in this work attention has been directed to wave-lengths below these.

* *Zeits. f. Physik*, xxxix. p. 562 (1926).

Method.

The author has recently developed a method * of obtaining spectra with very short exposures by the fusing of wires, and has applied it to the Schumann region as well as to the ultra-violet and visible regions. Among the properties characteristic of this source is a tendency for lines involving low terms (and particularly ground-terms) to be reversed in the fuse in air, and consequently this procedure was adopted in searching for the 1S_0 lines in the ultra-violet.

When the fuse is made horizontally in the vacuum grating spectrograph, there is a tendency to form long and short lines, the long lines being lines involving low-level terms. This property was used in seeking the 1S_0 lines in this region.

Since an account of the method and of the apparatus has been published before, it will not be repeated here.

Results.

(a) *Schumann Region*.—No long lines appeared in this region which did not belong to the spark spectrum. The long lines involved the ground-terms 2D_3 and 2D_2 of Ni II, which were found in this way †. It is conceivably possible that very low-level arc lines might under the conditions of the fuse *in vacuo* be completely absorbed, but this has so far not been observed in any other case. The spectrum was photographed as far as 1150 Å.U. Air-absorption prevented the examination going any further, owing to the poorness of the pumping system. (There was as compensation, however, the knowledge that all the lines in the region measured must be first-order lines.) An improved pumping system is being erected, and it is hoped to be able to go very much further.

(b) *Ultra-violet Region*.—In the fuse-spectrum in air there were many reversals, especially near 2300 and 2000 Å.U. These were measured in the spectrum of the arc between rods of pure nickel (supplied by Adam Hilger Ltd.) of 5 mm. diameter; the current was $4\frac{1}{2}$ amperes, and was maintained by an accumulator battery of 110 volts. The spectrograph was a small Hilger quartz instrument, giving a dispersion of about 12 Å.U. per mm. As standards for the calculation of Hartmann formulæ, the nickel spark lines measured by Shenstone ‡ were used. The fuse spectrograms were used

* Proc. Roy. Soc. A, cxvii. p. 88 (1927), and cxix. p. 249 (1928).

† Proc. Roy. Soc. (In process of publication.)

‡ Phys. Rev. xxx. p. 255 (1927).

merely to pick out the reversed lines in the arc spectrograms. The error is less than 0.1 Å.U. in the lines measured by the author. These lines are set out in Table II.

In the first column is the wave-length (above 2100 Å.U. the values of Hamm * have been adopted, and are indicated by H, while the other wave-lengths are the measurements made by the author). The second column gives the strength of the reversal (weak w, strong s), in the third the initials of previous observers of the reversal, in the fourth the wave-number, and in the last column the term-combination, using Bechert and Sommer's nomenclature. For the most part the initial terms in the transitions are terms not found before; these are indicated by giving their values in place of a letter, thus making the newly-found terms more obvious.

TABLE II.
Reversals in the Fuse-spectrum.

Wave-length.	Strength of reversal.	Previous observers.	Wave-number.	Terms.
2346.635 H	w	AJ, MLC	42601.2	$f_3^1 - u^1$
2345.545 H	s	AJ, MLC, Ma	42621.0	$f_4^1 - e^1$
2337.488 H	s	AJ, MLC	42767.8	$f_4^1 - l^1$
2329.974 H	w		42905.8	$f_2^1 - 45122.4$
2325.799 H	s	AJ, MLC	42982.8	$f_3^1 - r^1$
2324.653 H	w		43004.0	$\bar{d}_3^1 - 43208.8$
2322.688 H	w		43040.3	$\bar{d}_1^1 - 44753.4$
2321.387 H	s	MLC, MLML	43064.5	$f_2^1 - v^1$
2320.034 H	s	AJ, MLC, Ma	43089.5	$f_4^1 - n_e^1$
2317.158 H	w	AJ, MLC	43143.1	$f_3^1 - t_2^1$
2313.982 H	s	AJ, MLC	43202.3	$f_2^1 - \bar{f}_2^3$
2313.656 H	s		43208.3	$f_4^1 - 43208.3$
2312.338 H	w	AJ, MLC, Ma	43233.0	$f_3^1 - \bar{f}_3^3$
2310.955 H	s	AJ, MLC, Ma	43258.8	$f_4^1 - \bar{f}_4^3$
2306.420 H	w		43343.9	
2302.973 H	w		43408.8	$\bar{d}_1^1 - 45121.9$
2300.773 H	w	MLC	43450.3	$\bar{d}_3^1 - o_3^1$
2293.114 H	w		43595.4	$\bar{d}_2^1 - t_2^1$
2289.979 H	s	Ma	43655.0	$f_4^1 - o_8^1$
2288.388 H	w		43685.3	$\bar{d}_2^1 - \bar{f}_3^3$
2279.553 H	w		43856.7	

* *Z. wiss. Photogr.* xiii. p. 105 (1913).

TABLE II. (*continued*).

Reversals in Fuse-spectrum.

Wave-length.	Strength of reversal.	Previous observers.	Wave-number.	Terms.
2273·85	w		43966·6	
2270·206 H	w		44035·2	$a^4\bar{F}_4 - a^4\bar{G}_5$ spk.
2244·246 H	w		44544·5	$\bar{d}_3^1 - 44749·3$
2216·459 H	w		45102·9	$a^4\bar{F}_5 - a^4\bar{G}_6$ spk.
2201·529 H	w		45408·7	$\bar{d}_1^1 - 47121·8$
2183·334 H	w		45787·2	$f_3^1 - 47119·4$
2095·57	w		47704·5	
2094·94	w		47718·8	$\bar{D}_2^1 - 51128·8$
2088·90	w		47856·8	$\bar{d}_2^1 - 48736·6$
2082·94	w		47993·6	$f_3^1 - 49325·8$
2069·54	w		48304·4	$\bar{d}_1^1 - 50017·5$
2068·89	s		48319·6	
2064·30	w		48427·0	$\bar{d}_1^1 - 50140·1$
2063·58	s		48443·9	$\bar{d}_2^1 - 49323·7$
2059·97	s		48528·8	$\bar{d}_3^1 - 48733·6$
2055·44	s		48635·8	$f_2^1 - 50852·4$
2052·19	s		48712·7	
2050·91	w		48743·2	$f_4^1 - 48743·2$
2047·35	s		48828·0	
2041·17	w		48975·8	$\bar{d}_1^1 - 50688·9$
2035·15	s		49120·6	$\bar{d}_3^1 - 49325·4$
2034·51	s		49136·0	$\bar{d}_1^1 - 50849·1$
				$\bar{d}_2^1 - 50015·8$
2026·66	s		49326·3	$f_4^1 - 49326·3$
2025·91	s		49344·6	
2025·41	w		49356·7	$f_3^1 - 50688·9$
2014·12	s		49633·4	$\bar{d}_1^1 - 51346·5$
2007·74	w		49791·0	$f_3^1 - 51123·2$
2007·05	w		49808·1	$\bar{d}_2^1 - 50687·9$
				$\bar{d}_3^1 - 50012·9$
2001·77	s		49939·5	$\bar{d}_3^1 - 50144·3$
2000·46	s		49972·2	$\bar{d}_2^1 - 50852·0$
(vac.)				
1994·40	w		50140·4	$f_4^1 - 50140·4$
1990·18	s		50246·7	$\bar{d}_2^1 - 51126·3$
1889·28	w	MLO	50269·4	
1981·48	w		50467·1	$\bar{d}_2^1 - 51346·9$

TABLE II. (*continued*).
Reversals in Fuse-spectrum.

Wave-length.	Strength of reversal.	Previous observers.	Wave-number.	Terms.
1976·87	s	MLC	50585·0	$\bar{d}_3^1-50789·8$
1974·53	w		50644·7	$\bar{d}_3^1-50849·5$
1968·92	w		50789·3	$f_4^1-50789·3$
1963·89	w		50919·4	$\bar{d}_3^1-51124·2$
1882·7	w		53115	
1873·1	vs		53386	
1852·8	s		53971	
1840·4	s		54337	

H, Hamm; AJ, Angerer and Joos*; MLC, McLennan and Cooley†; Ma, Majumdar; MLML, McLennan and McLay‡.

The last four lines were difficult to measure exactly, owing to their broadness as well as to their position at the end of the spectrum. Confirmation of three of the new terms suggested above was obtained from Hamm's list, in which the following lines appear (with the exception of the fourth, measured by the author):—

Wave-length (air).	Wave-number (vac.).	Terms.
2259·550	44242·9	$\bar{d}_2^1-45122·7$
2396·637	41712·3	$\bar{D}_2^1-45122·3$
2278·759	43870·0	$\bar{d}_2^1-44749·8$
2302·48 M	43418·0	$f_3^1-44750·2$
2350·472	42531·7	$f_2^1-44748·3$
2226·296	44903·6	$f_2^1-47120·2$
2287·086	43710·2	$\bar{D}_2^1-47120·2$

Some of the terms are a bit doubtful, particularly 48734, 50013, and 50140.

Conclusion.

It will be seen that it has been possible to account for the majority of the reversed lines. It is not possible to fit in a 1S_0 ground-term in the region of the spectrum investigated, and so the term 3F_4 must still be regarded as the lowest found in the spectrum of Ni I.

* *Ann. der Phys.* lxxiv. p. 743 (1924).

† *Trans. Roy. Soc. Can., Sect. III.* p. 349 (1926).

‡ *Trans. Roy. Soc. Can., Sect. III.* p. 89 (1925).

Summary.

The ground-term of Ni I empirically is a term 3F_4 . Doubt exists that this is the ground-term to be expected theoretically; it might be a 1S_0 term.

Fuse-spectra in air in the ultra-violet and *in vacuo* in the Schumann region have been examined. Many reversed lines in the former region have been found, but most of them can be accounted for as transitions to low levels already known, from middle terms already known and from new middle terms. In the Schumann region no long lines occur which could be attributed to the arc; they all appear to belong to the ground-terms 2D_3 and 2D_2 of Ni II.

It is concluded that the hypothetical term 1S_0 must give rise to lines below the region examined, if the term exists at all.

Physics Department,
University College, Leicester.
7th October, 1928.

CXVIII. *General Solution of $\nabla^2\psi=\omega$.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN my paper "General Solution of $\nabla^2\psi=\omega$," which appeared on pp. 241 *et seq.* of the August 1928 issue of this Magazine, I regret to notice the occurrence of some errors, chiefly my own. May I beg space to point out the corrections?

On p. 245, bottom line, read " $d\theta_{n-1}$," not " $d\theta_n$."

„ „ footnote, „ „ " r_n ," not " ν_n ."

„ p. 246, end of l. 2 fr. bottom, supply " θ_n ."

„ p. 248, in equation (12), " $d\theta_s$ " comes *after* bracket.

„ p. 249, l. 7, read " $dV_{n-1}^2=J_sJ_s\{d\theta_{n-1}\}^2$."

„ p. 250, l. 6, „ „ " $R=\infty$," not " $n=\infty$."

„ „ end of l. 2 fr. bottom, read " du_4 ."

„ p. 251, beginning of l. 2 fr. bottom, read " $\frac{\dot{v}}{c^2}$ " not " $\frac{v}{c^2}$ " „

„ p. 252, end of l. 1, "along the normal to the two-"

On p. 253, l. 1, read " $4c \int \Sigma R dv$," not " $4c \int \frac{\Sigma R}{r} dv$ ".

„ „ l. 8, „ " $\phi\omega$," not " ω ."

„ „ l. 20, „ " $\left(\frac{1}{r}\right) F(ct_1 + r)$,"
not " $\left(\frac{1}{r}\right) F\left(t_1 + \frac{r}{c}\right)$."

„ „ l. 22, „ " $\left(\frac{1}{2r}\right) f(ct + r)$,"
not " $\left(\frac{1}{2rc}\right) f\left(t_1 + \frac{r}{c}\right)$."

„ p. 254, l. 3, „ " $\xi(z)f(z)$," not " $f(z)$."

„ p. 255, l. 16, „ " $U_1 \frac{\partial y}{\partial u_1}$," not " $U_1 \frac{\partial y}{\partial u_2}$."

„ „ l. 5 fr. bottom, read " $\int_0^{2\pi} y \frac{\partial x}{\partial \theta} \cdot d\theta$."

„ p. 257, l. 9, read " $2\pi\psi_A$," not " ψ_A ."

I am sorry to give you all this trouble, mainly through negligence on my part, but to any who care to read the paper these corrections must seem necessary.

Thanking you for publishing this note,

Yours faithfully,

97 Thornbury Road,
Osterley Park,
Middlesex.

ARTHUR J. CARR.

CXIX. *On the Buckling of a Thin Circular Plate by Heat.*
By F. E. RELTON, B.A., B.Sc., Imperial College*.

Summary.

THE circular plate is assumed to be thin and at uniform temperature. The analysis is limited by the fact that the temperature must not generate stresses that exceed the

* Communicated by Prof. S. Chapman, F.R.S.

elastic limit, and that the relative dimensions are bounded in order that buckling may occur before the elastic limit is reached. This latter justifies the ignorance of the most awkward term in the equations of equilibrium, of which three are deduced from first principles. As two of these are sufficient, the two most suitable are chosen. Their exact solution is impracticable, and recourse is had to power series. By substitution and a comparison of coefficients, there results a number of equations which are two in defect of the number of coefficients involved at any stage of the work. The deficiency is made up by the boundary conditions, including the peripheral strain due to heat. All the unknowns are expressible in terms of two quantities which are connected with the relative dimensions of the disk and its central curvature. By giving values to the one the other can be determined; hence all the coefficients can be found and the problem completely solved. The method is inverse inasmuch as the appropriate temperature is deduced from the configuration of the disk. Full discussion of the clamped plate necessitates computing rather many terms to a high degree of accuracy; the method is much more efficacious when applied to the unclamped plate.

(1) **W**E consider a thin, plane, circular disk whose temperature and thickness are uniform and whose periphery is prohibited from radial movement. If the temperature of the disk be raised, it is a contingency that the disk will buckle; the present paper is an attempt to determine the deflexions and stresses engendered when buckling occurs.

(2) At the outset we are called upon to examine two possibilities which may limit the validity of the analysis. In the first place, the peripheral transverse strain (*i. e.* perpendicular to the radius in the plane of the disk) is $\alpha\theta$, determined by the rise in temperature θ and the coefficient α of expansion of the material. So long as the disk does not buckle, the radial strain is this same quantity $\alpha\theta$, being somewhat less when buckling occurs. Thus, before buckling, we have a uniform state of plane stress of magnitude $E\alpha\theta/(1-\sigma)$, and the analysis becomes the less reliable the more closely this quantity approaches the elastic limit f . We have a provisional upper limit for the temperature θ in the relation $\theta = f(1-\sigma)/E\alpha$.

(3) Coming to figures *, we have in c.g.s. units :

	$10^{-8} . f.$	$10^{-11} . E.$	$\sigma.$	$10^6 . a.$	$\theta^{\circ} . C.$
Steel.....	30	22	0.25	10	100
Copper	0.5	10	0.34	16	2
Aluminium ...	5	7	0.34	23	20

the computed approximate value of θ in degrees centigrade being given in the last column. It appears that the range of validity varies considerably from one metal to another.

(4) The second limitation arises from the necessity of the elastic limit not being reached before the buckling load becomes critical, a criterion which furnishes a bound to the relative dimensions of the disk. Taking a clamped disk of radius c and thickness $2h$, the "buckling" thrust T per unit length of periphery is given † by

$$T = 2Eh^3\gamma^2/3c^2(1-\sigma^2),$$

where γ is the least root of $J_1(\gamma)=0$, to be taken as 3.832. The condition that T is less than $2hf$ gives

$$(c/h)^2 > E\gamma^2/3f(1-\sigma^2).$$

Using the previous figures, this provides a lower limit to c/h of approximately 60, 330, 90 for steel, copper, and aluminium respectively.

(5) For an unclamped plate the $\gamma=3.832$ is replaced by the smallest root of $\gamma J_0(\gamma)=(1-\sigma)J_1(\gamma)$, which may be taken ‡ as 2.017 when σ is a quarter. The corresponding minimum values of c/h will accordingly be about half those given above.

(6) Coming now to the analysis, we see that the solution will be symmetrical, there being only one independent variable r , the distance from the centre; we shall accordingly use primes to denote differentiations with respect to r . The stress \widehat{zz} perpendicular to the faces of the disk vanishes at both faces, and since the disk is thin will be ignored throughout.

(7) We conceive a point on the middle surface whose coordinates are $r, \phi, 0$ to be moved to $\bar{r}+\bar{u}, \phi, w$, so that

* "Recueil de Constantes Physiques," Soc. Fran. de Phys.

† G. H. Bryan, Proc. Lond. Math. Soc. xxii. (1890).

‡ Precott 'Applied Elasticity,' p. 488.

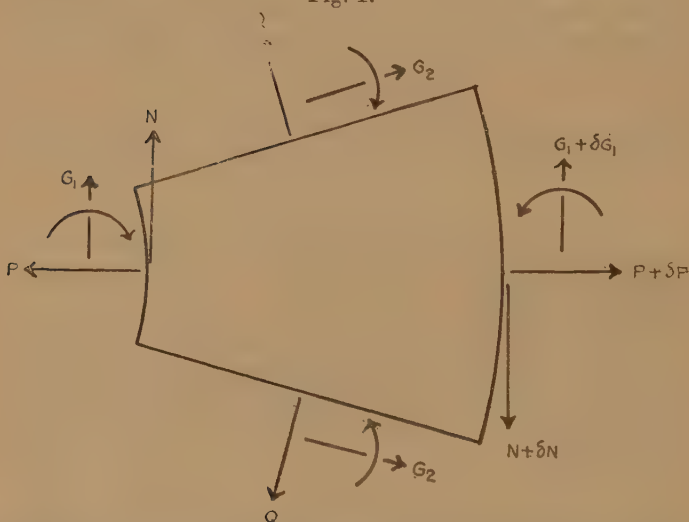
w is the deflexion. In the principal direction $\phi = \text{constant}$ we have the length element δr becoming $\{(\delta r + \delta u)^2 + \delta w^2\}^{1/2}$, so that the strain $e_{rr} = u' + \frac{1}{2}w'^2$. In the other principal direction $r = \text{constant}$ we have the length element $r \cdot \delta \phi$ becoming $(r + u) \cdot \delta \phi$, so that the strain $e_{\phi\phi} = u/r$. These lead to

$$\left. \begin{aligned} P_1 - \sigma Q_1 &= E(u' + \tfrac{1}{2}w'^2), \\ Q_1 - \sigma P_1 &= Eu/r, \end{aligned} \right\} \dots \dots (1)$$

where P_1, Q_1 are the tensile stresses in the middle surface. For the principal curvatures we have

$$\left. \begin{aligned} 1/\rho_1 &= w''(1 + w'^2)^{-3/2} = w'', \\ 1/\rho_2 &= w'/r(1 + w'^2)^{1/2} = w'/r \end{aligned} \right\} \dots \dots (2)$$

Fig. 1.



along and perpendicular to the meridian respectively. The assumption is made that w' is everywhere small, though w is not necessarily small compared with the thickness $2h$. We shall further assume that the tensile stresses have a straight-line distribution through the thickness; this is tantamount to ignoring powers of h above the second in comparison with h . We then have $P = 2hP_1$, $Q = 2hQ_1$, where P, Q denote the force per unit length of edge, acting radially and transversely respectively.

(8) In the diagram (fig. 1) showing the arrangement of forces and couples we conceive the disk to be concave

upwards, whilst w is measured upwards above the level of the centre. Hence *

$$G_1 = \frac{2}{3} \cdot \frac{Eh^3}{1-\sigma^2} \left(\frac{1}{\rho_1} + \frac{\sigma}{\rho_2} \right), \quad G_2 = \frac{2}{3} \cdot \frac{Eh^3}{1-\sigma^2} \cdot \left(\frac{1}{\rho_2} + \frac{\sigma}{\rho_1} \right). \quad (3)$$

For the equations of equilibrium we have, by normal resolution,

$$\frac{d}{dr} (Nr \cdot d\theta) dr = Pr \cdot d\theta \cdot \frac{dr}{\rho_1} + Q \cdot dr \cdot \frac{r \cdot d\theta}{\rho_2}$$

or

$$P/\rho_1 + Q/\rho_2 = d(Nr)/r \cdot dr. \quad (4)$$

Along the meridian tangent

$$\frac{d}{dr} (Pr \cdot d\theta) dr + (Nr \cdot d\theta) \cdot \frac{dr}{\rho_1} = (Q \cdot dr) d\theta$$

or

$$Nr/\rho_1 = Q - d(Pr)/dr. \quad (5)$$

The binormal naturally leads to nothing owing to the symmetry, but moments about the inner curved edge give

$$\frac{d}{dr} (G_1 r \cdot d\theta) dr = (G_2 \cdot dr) d\theta + (Nr \cdot d\theta) dr$$

or

$$Nr = d(G_1 r)/dr - G_2. \quad (6)$$

Denoting by E_1 the quantity $2Eh^3/3(1-\sigma^2)$, equations (2) and (3) give

$$\left. \begin{aligned} G_1 &= E_1(w'' + \sigma w'/r), \\ G_2 &= E_1(w'/r + \sigma w''), \end{aligned} \right\} \quad (7)$$

whence equation (6) becomes

$$N = E_1 d(\nabla^2 w)/dr. \quad (8)$$

(9) It will be observed that, if in equation (4) we put $P=Q=\text{constant}$, the equation becomes the well-known equation for the critical buckling load †:

$$P \nabla^2 w = E_1 \nabla^4 w.$$

Further, if we can ignore the left side of equation (5), it becomes possible to express P, Q in terms of a single function U so that $P=U'/r, Q=U''$, in which case the elimination of u from equations (1) gives

$$r \nabla^4 U + 2hEw'w'' = 0;$$

* Love, 'Elasticity,' 4th ed. p. 464.

† *Vide* Bryant, *l. c.*

whilst equation (4), in the presence of a pressure p normal to one face of the disk, becomes *

$$d(U'w')/r \cdot dr = E_1 \nabla^4 w + p.$$

The exact solution of these two well-known simultaneous, non-linear differential equations may be ruled out as impracticable †, and matters are not made easier by the absence of p with the retention of the left side of equation (5).

(10) The equations (1) can be replaced by

$$\left. \begin{aligned} P(1-\sigma^2) &= 2hE(u' + \sigma u/r + \tfrac{1}{2}w'^2), \\ Q(1-\sigma^2) &= 2hE(u/r + \sigma u' + \tfrac{1}{2}\sigma w'^2). \end{aligned} \right\} \quad . \quad . \quad (9)$$

Using these and equation (8), the equilibrium equations (4) and (5) respectively become

$$(u' + \tfrac{1}{2}w'^2)(w'' + \sigma w'/r) + (\sigma w'' + w'/r)u/r = h^2 \nabla^4 u/3, \quad (10)$$

$$u/r - u' - ru'' = \tfrac{1}{2}(1-\sigma)w'^2 + rw'w'' + \tfrac{1}{3}h^2 w'' rd(\nabla^2 w)/dr, \quad . \quad . \quad (11)$$

and the problem before us now is to solve these two equations.

(11) The most hopeful procedure lies in the adaptation of the method employed by Hencky ‡ in a similar connexion. From the symmetry of the meridian curve we propose to express w as an even function in ascending powers of r , vanishing at the origin. Using s to denote the ratio r/c , where c is the radius of the disk, we accordingly take

$$\left. \begin{aligned} w' &= a_1 s + a_3 s^3 + a_5 s^5 + \dots, \\ cw'' &= a_1 + 3a_3 s^2 + 5a_5 s^4 + \dots, \\ c^2 w''' &= 3.2a_3 s + 5.4a_5 s^3 + \dots, \end{aligned} \right\} \quad . \quad . \quad (12)$$

where the a 's are dimensionless constants. Equation (11) then shows that u is an odd function of r ; we accordingly take

$$\left. \begin{aligned} u/r &= b_0 + b_2 s^2 + b_4 s^4 + \dots, \\ u' &= b_0 + 3b_2 s^2 + 5b_4 s^4 + \dots, \\ ru'' &= 3.2b_2 s^2 + 5.4b_4 s^4 + \dots, \end{aligned} \right\} \quad . \quad . \quad (13)$$

* Cf. Föppl, *Vorl. ü. tech. mech.* Bd. v. § 24.

† Cf. Th. v. Kármán, *Ency. d. Math. Wiss.* iv. 4, c. art. 27.

‡ *Zeitsch. für Math. u. Phys.* lxiii. p. 311 (1914).

where the b 's are dimensionless. The method consists in substituting for the various differentials of u and w in equations (10) and (11). A comparison of the coefficients of corresponding powers of s then supplies two sets of relations between the a 's and b 's. We thus obtain two expressions for any particular b in terms of the a 's, and the equivalence of these two expressions furnishes a relation connecting the a 's alone.

(12) It is evident *à priori* that the number of such relations available at any stage of the work must be in defect of the number of a 's present; otherwise the a 's, and hence the b 's, would be determinable, leaving no latitude for the fulfilment of boundary and other conditions. In practice it eventuates that the defect is two, and these are supplied from our knowledge: first, that the transverse strain $u/r = \alpha\theta$ at the boundary $r=c$; second, the condition which varies according as the periphery is clamped or not. The number of available relations is then theoretically sufficient to solve the problem to any required degree of approximation.

(13) In actual fact, the degree of approximation obtainable in general terms is severely limited; for since the differential equations to be solved are non-linear, the resulting algebraical equations which determine the a 's are also non-linear. From this it follows that, even if u and w are presumed to be given with sufficient accuracy by quite a small number of terms in their equivalent expansions, the eliminant that determines any particular a soon transcends the fourth degree. The coefficients in this eliminant are not wholly arithmetical, being, in fact, dependent on σ and the ratio h/c , so that very soon the a 's are no longer determinable.

(14) If the relative dimensions and the values of the physical constants for the disk are known, the above-mentioned eliminants have purely arithmetical coefficients and the a 's can be determined as accurately as desired. But a further difficulty here arises. Each a will be susceptible of several values, and the resulting expressions for u and w are not unique. This, of course, is to be expected, since the equilibrium configuration of the disk is, theoretically at least, not unique. There would remain, in such a case, the task of determining the conditions appropriate to each particular solution.

(15) Reverting now to the analysis, a slight modification is desirable before we carry our proposal into effect. We see from equations (4) and (5) that we can eliminate Q and derive a relation between P and N ; but this relation is more readily found from statical considerations. If we consider the equilibrium of a concentric circular portion of the disk and resolve in the axial direction, we get quite simply

$$N = Pw' \dots \dots \dots (14)$$

There are certain advantages in using equation (14) in preference to equation (10), and this we shall do in conjunction with equation (11).

(16) Since the quantity $(h/c)^2$ is of frequent occurrence, we shall denote its value by n , a number whose magnitude is 10^{-3} or less. The relations furnished by equation (14) may then be succinctly written

$$(\mu^2 - 1)a_\mu n/3 = \Sigma a_p b_q (q + 1 + \sigma) + \frac{1}{2} B(\overline{\mu - 2} : 3), \dots (15)$$

where $p + q = \mu - 2$ and $B(\overline{\mu - 2} : 3)$ denotes the aggregate of coefficients of order 3 and weight $\overline{\mu - 2}$ in w'^3 or $(\Sigma a)^3$, the weight of any letter being its suffix.

(17) Equation (11) furnishes no information concerning b_0 , but it provides relations which may be summarized as

$$(1 - \overline{\nu + 1}^2)b_\nu = \frac{1}{2}(\nu + 1 - \sigma)A(\nu : 2) + nc(\overline{\nu + 2} : 2)/3, \dots (16)$$

where $A(\nu : 2)$ is the aggregate of coefficients of order 2 and weight ν in w'^2 or $(\Sigma a)^2$, and $c(\overline{\nu + 2} : 2)$ is the aggregate of coefficients of order 2 and weight $(\nu + 2)$ in $w'd(\nabla^2 w)/dr$.

(18) We know that, at the periphery where $r = c$ and s is unity, the magnitude of the transverse strain u/r is $\alpha\theta$; hence from equation (13) we have

$$-\alpha\theta = b_0 + b_2 + b_4 + \dots = \Sigma b, \dots \dots \dots (17)$$

the negative sign on the left being necessary for compression.

The Clamped Plate.

(19) When the plate is clamped round the periphery, we have w' zero when s is unity, so that from equation (12) we have

$$0 = a_1 + a_3 + a_5 + \dots = \Sigma a. \dots \dots \dots (18)$$

A possible solution is evidently to have all the a 's zero

together with all the b 's except b_0 , whose value is then $-\alpha\theta$. In this case w is everywhere zero and

$$P=Q=-2hE\alpha\theta/(1-\sigma),$$

which is simply the particular case where the heat-stresses are not great enough to cause buckling.

(20) For the general case where buckling occurs we are provided with an infinite number of non-linear equations for the determination of an infinite number of unknowns, so that we necessarily adopt some method of approximation. At the outset it appears from equation (16) that it would be safe to omit the last term on the right in comparison with the others in virtue of the smallness of n . This is equivalent to omitting the last term on the right in equation (11), or ignoring the left side of equation (5). Further, if we use k to denote the ratio a_3/a_1 , it becomes possible to express all the unknowns in terms of a_1 and k . Thus, using equations (15) and (16) alternately, we deduce as the first few values

$$\begin{aligned} b_0 &= 8nk/3(1+\sigma), & b_4 &= -(5-\sigma)a_1^2k/24, \\ b_2 &= -(3-\sigma)a_1^2/16, & a_7 &= a_1k^3/18 - a_1^3k(1-\sigma^2)/128n, \\ a_5 &= a_1k^2/3 - (1-\sigma^2)a_1^3/128n, \\ b_6 &= -\frac{7-\sigma}{96}\left(\frac{5}{3}a_1^2k^2 - \frac{1-\sigma^2}{64n}a_1^4\right), \end{aligned}$$

whence b_3 , a_9 , and so on can be determined in succession.

(21) The quantity a_1 has a physical meaning; we see from equation (12) that it is the common value, at the centre, of the ratio (radius of plate)/(radius of curvature). This ratio is necessarily small in practice, and closer inspection of the above and succeeding values of the first few a 's and b 's shows that there are considerable advantages in equating a_1 to $\beta\sqrt{n}$. It eventuates that a_{2t+1}/a_1 becomes homogeneous of degree t in k and β , as also does $b_{2(t-1)}/n$. For a known value of σ the condition (18) is then expressible in terms of k and β with purely arithmetical coefficients, so that by giving values to the one the other can be determined. In this manner the a 's can be expressed as multiples of \sqrt{n} , and the b 's as multiples of n . The success of the method depends on the degree of reliability with which the modified condition (11) can be solved.

(22) For a plate of known size the deflexion can be computed from the integrated form of equation (12), while

the corresponding value of $\alpha\theta$ is given by equation (17). The method will, of course, not immediately give the deflexion corresponding to a specific value of $\alpha\theta$; this would have to be deduced by interpolation from computed values.

(23) Making the substitution mentioned in § 21, and using δ as a convenient abbreviation for the quantity $\beta^2(1-\sigma^2)/128$, we derive from equations (15) and (16) the following values :—

$$\left. \begin{aligned} a_1/\beta \sqrt{n} &= 1, & a_3/\beta \sqrt{n} &= k, & a_5/\beta \sqrt{n} &= k^2/3 - \delta, \\ a_7/\beta \sqrt{n} &= k^3/3.6 - k\delta, \\ a_9/\beta \sqrt{n} &= k^4/3.6.10 - 29k^2\delta/60 + 2\delta^2/5, \\ a_{11}/\beta \sqrt{n} &= k^5/3.6.10.15 - 143k^3\delta/900 + 38k\delta^2/75, \\ a_{13}/\beta \sqrt{n} &= k^6/3.6.10.15.21 - 38k^4\delta/945 \\ &\quad + 47k^2\delta^2/140 - 64\delta^3/525, \\ a_{15}/\beta \sqrt{n} &= k^7/3.6.10.15.21.28 - 29k^5\delta/28.126 \\ &\quad + 1702k^3\delta^2/75.147 - 158k\delta^3/525, \end{aligned} \right\} \quad (19)$$

and so on, together with

$$\left. \begin{aligned} b_0/n &= 8k/3(1+\sigma), & b_2/n &= -\beta^2(3-\sigma)/16, \\ b_4/n &= -k\beta^2(5-\sigma)/24, \\ \frac{b_6}{n} &= -\frac{(7-\sigma)}{96} \beta^2 \left(\frac{5}{3} k^2 - 2\delta \right), \\ \frac{b_8}{n} &= -\frac{(9-\sigma)}{80} k\beta^2 \left(\frac{7}{11} k^2 - 2\delta \right), \\ \frac{b_{10}}{n} &= -\frac{(11-\sigma)}{240} \beta^2 \left(\frac{7}{30} k^4 - \frac{109}{30} k^2\delta + \frac{9}{5} \delta^2 \right), \\ \frac{b_{12}}{n} &= -\frac{(13-\sigma)}{168} k\beta^2 \left(\frac{11}{450} k^4 - \frac{232}{225} k^2\delta + \frac{143}{75} \delta^2 \right). \end{aligned} \right\} \quad (20)$$

There is no intrinsic difficulty in extending either of these series; the main deterrent is the tedium, which is the inevitable concomitant of lengthy computations.

(24) The above values show that the condition (18) is always satisfied by a zero value of β , which corresponds to the physical fact that the undeflected state is always a

possible equilibrium position. Apart from this value the condition can be written in the expressive form:

$$1+k+\frac{k^2}{3}+\frac{k^3}{3.6}+\dots$$

$$= \delta \left(1+k+\frac{29}{60}k^2+\dots \right) - \delta^2 \left(\frac{2}{5}+\frac{38}{75}k+\dots \right)$$

$$+ \delta^3 \left(\frac{64}{525}+\frac{158}{525}k+\dots \right) - \dots, \quad (21)$$

where the left side is independent of whatever value of σ may be adopted. By making β infinitesimal we have the corresponding deflexion, from the integrated form of equation (12), expressible as

$$w = ca_1 \left(\frac{s^2}{2} + \frac{s^4}{4}k + \frac{s^6}{6} \cdot \frac{k^3}{3} + \frac{s^8}{8} \cdot \frac{k^3}{3.6} + \dots \right)$$

$$= ca_1 \{ J_0(s\sqrt{-8k}) - 1 \} / 4k. \quad \dots \quad (22)$$

This succinct form of the result is by no means fortuitous, but is a necessary consequence of its mode of derivation; such a choice of β makes all the α 's infinitesimal and likewise the deflexion. The analysis accordingly reverts to that for determining the critical buckling load, whence the result stated above. It appears that the quantity $\sqrt{-8k}$ is what we have previously called γ , to be taken as 3.832; the appropriate value of k is accordingly -1.835 , whilst the left side of equation (21) is always $J_1(2\sqrt{-2k})/\sqrt{-2k}$, which is convenient for computation.

(25) In illustration of the remarks in § 21, let us take σ to be $1/3$, so that δ becomes $(\beta/12)^2$, which we may denote by η . Equation (21) then becomes

$$\frac{J_1(2\sqrt{-2k})}{\sqrt{-2k}} = \eta \left(1+k+\frac{29}{60}k^2+\dots \right) - \eta^2 \left(\frac{2}{5}+\frac{38}{75}k+\dots \right)$$

$$+ \eta^3 \left(\frac{64}{525}+\dots \right) - \dots$$

If we assume that the deflexion of the plate is given with sufficient accuracy by a series terminating at the sixteenth power of the radius inclusive, then, with $k=-1.805$, we have

$$\sqrt{-2k} = 1.9 \quad \text{and} \quad J_1(2\sqrt{-2k})/\sqrt{-2k} = 0.006748.$$

The above equation then becomes

$$0.006748 = 0.10461 \eta + 0.32850 \eta^2 - 0.42128 \eta^3,$$

whence η is 0.0555 and β is 2.827. From equations (19) we have for the values of the a 's, taken in order: +1, -1.8050, +1.0303, -0.2272, -0.0273, +0.0419, -0.0197, +0.0050, each multiplied by $\beta \sqrt{n}$. According to equation (18), the value of Σa should be zero; with the present approximation the sum totals -0.0010.

(26) From equations (20) we have the following values of the b 's, taken in order, each being multiplied by n : -3.61, -1.3320, +2.8046, -2.9514, +1.8061, -0.6482, +0.0858. To these may be added +0.0514, -0.0421, as the values of b_{14} , b_{16} respectively, computed from equation (16). The condition (17) gives $\alpha\theta = 3.836 n$; for a plate whose diameter is a hundred thicknesses we have $n = 10^{-4}$, so that the present instance would cover the case of an aluminium plate heated about 16.7°C .

(27) By integration of equation (12) we have

$$\frac{w}{c} = \frac{s^2}{2} a_1 + \frac{s^4}{4} a_3 + \frac{s^6}{6} a_5 + \dots,$$

so that the central deflexion, obtained by putting s equal to unity, is given by

$$w = ca_1 \left(\frac{1}{2} + \frac{a_3}{a_1} \cdot \frac{1}{4} + \frac{a_5}{a_1} \cdot \frac{1}{6} + \dots \right).$$

As a_1 is $\beta \sqrt{n}$, and h is $c \sqrt{n}$, we can replace ca_1 by βh . For the figures given above, the central deflexion evaluates to 0.542 h , or little more than a quarter of the thickness, which is, perhaps, surprisingly small in view of the fact that the material is not far removed from its elastic limit.

(28) It must be regarded as unfortunate that the a -series and b -series are not more rapidly convergent; it greatly impedes the discussion of associated phenomena. For example, the clamped disk is necessarily inflected, and if we seek to inquire how the greater deflexion affects the position of this inflexion, we do so by equating w'' to zero. With the present figures we solve the resulting equation of the fourteenth degree in s (actually the seventh degree in s^2), and we obtain $s^2 = 0.232(3)$, so that s is 0.482. The corresponding value for the critical buckling load when the deflexion is infinitesimal is derived from $J_1(x) = xJ_0(x)$, where x is 3.8317 s . This gives x as 1.8412 and s as 0.4805,

whence it appears that the effect of the greater deflexion is to move the inflexion further from the centre. But the labour in obtaining the result is considerable and the verdict not very emphatic.

(29) Of the two series, the b -series is the less satisfactory. If we seek to compare the principal stresses at the periphery, we can do so by using equations (1) and (13). Since w' is zero we have

$$\frac{P - \sigma Q}{Q - \sigma P} = \frac{b_0 + 3b_2 + 5b_4 + \dots}{b_0 + b_2 + b_4 + \dots}.$$

With the values in § 26 this becomes

$$\frac{P - Q/3}{Q - P/3} = \frac{3.9474}{3.8356}.$$

According to this, $P \propto 5.8066$ and $Q \propto 5.7238$ whereas, had the plate remained undeflected at this temperature, we should have had $P = Q \propto 5.7534$, which would make it appear that one effect of buckling was slightly to increase the radial force and diminish the transverse force. Such an improbable conclusion would be warranted only by proceeding to a much higher degree of approximation.

(30) It may be noted, finally, that equation (11) provides a severe check on the computed values of the b 's. For since the last term on the right has been ignored and w' is zero at the periphery, we have from equation (13), after removing 8 as a factor,

$$b_2 + 3b_4 + 6b_6 + 10b_8 + 15b_{10} + \dots \equiv 0.$$

The last of our computed values is $b_{16} = -0.0421$, and with its appropriate factor, $36b_{16} = -1.5156$. The difficulty of getting a close fit with a series subject to such violent oscillations is evident. As an indication of the convergence of this series to zero, we may treat it as "summable (C 1)" by Cesàro's method*. The values of S_ν for $\nu = 1, 4, 6, 8$, are $-1.3320 + 0.6394, -0.0363, +0.0214$ respectively.

The Unclamped Plate.

(31) For the unclamped plate the condition (18) is replaced by the fact that G_1 is zero at the periphery, so that from equations (7) and (12) we have

$$\Sigma a_r(\tau + \sigma) = 0, \quad . \quad . \quad . \quad . \quad . \quad (23).$$

* *Vide* Whittaker & Watson, 'Modern Analysis,' 2nd ed. 8.43.

$\frac{1}{C} \cdot \frac{\Delta L}{L} = l$, and $\frac{1}{C} \frac{\Delta \eta}{\eta} = r$, it follows then that $H_{\infty} = l_{\infty} + r_{\infty}$. If the change of viscosity on dissolving the metal in mercury be small, it is found that $\left(\frac{1}{C} \cdot \frac{\Delta L}{L}\right)_{\infty}$ or l_{∞} has approximately the same value for all such metals.

The solution of most metals in mercury increases the conductivity, and the only exceptions to the rule are the alkali metals. According to Skaupy* these exceptions can be explained by the experimental work of Feninger†, who found that the internal friction of mercury is very much increased by solution of the alkali metals in it. Therefore, when comparing all metals, it is necessary to consider the values of $(l_{\infty} + r_{\infty})$, and not l_{∞} alone.

Skaupy further showed that $\frac{H_{\infty} - H}{C}$ is constant, and therefore if the variation of viscosity can be neglected the value of $\frac{l_{\infty} - l}{C}$ should be constant.

In the present work the values of l were determined for copper and gold amalgams of various concentrations at temperatures between 0° and 300° C., and the values of l_{∞} and $\frac{l_{\infty} - l}{C}$ evaluated in each case.

The full expressions could not be calculated owing to the lack of data concerning the viscosities of the amalgams used in the present investigations.

In order to calculate the values of l it was necessary to determine the resistance of a mercury column of the same dimensions as the amalgam column, and under exactly the same conditions. The values of the electrical conductivities of pure mercury at various temperatures between 0° and 300° C., deduced from these experiments, agreed within the limits of experimental error with those obtained by Williams‡ and Edwards§.

EXPERIMENTAL ARRANGEMENT.

The resistivities and conductivities of pure mercury and of the various amalgams at various temperatures were determined by measuring the electrical resistance of a fine

* *Loc. cit.*

† H. Feninger, 'Die Electriche Leitfähigkeit und innere Reibung Verdünnter Amalgame,' Freiburg, 1914.

‡ E. J. Williams, *Phil. Mag.*, Sept. 1925, p. 589.

§ T. I. Edwards, *Phil. Mag.*, July 1926, p. 1.

cylindrical column of the conductors enclosed in a quartz capillary tube.

It is only necessary to give a brief account of the method, as it does not differ appreciably from that previously described by Williams * and Edwards †.

The instrument employed to measure the resistance of the column was a Callendar-Griffiths bridge, which was used in conjunction with a sensitive moving coil galvanometer capable of detecting a current of 10^{-9} ampere. The resistance could be measured accurately to 0.0005 ohm, which at high temperatures corresponded approximately to a change of 0.1°C . in the temperature of the mercury or amalgam column, and to a change of 0.17°C . at low temperatures. In the first place, the Callendar-Griffiths bridge was calibrated in the usual way, and the relative values of the bridge resistances in terms of the largest one determined. A knowledge of the correct absolute values of these bridge resistances is not necessary for the determination of either the temperature coefficient of resistivity, or even the absolute values of the resistivities of mercury and the amalgams. The standard value of the resistivity of mercury at 0°C . is taken to be 94074×10^{-9} , and this corresponds to a known value of the resistance of the given mercury column determined at the same temperature. It is then possible to calculate the resistivity at any temperature from the temperature coefficient. The method employed in calculating the resistivities of the various amalgams will be described later. The current entered the mercury or amalgam contained in the quartz tube by means of specially constructed leads which have been previously described ‡, and the resistance of the column was determined by subtracting the resistance of the leads, which was determined separately, from the total resistance measured. In the case of gold and copper amalgams, which oxidize only to small extent in air, the vertical limbs of the quartz tube carrying the leads were open to the atmosphere.

Method of Heating, and of Measuring Temperature.

The resistances of the mercury and amalgams were measured at several temperatures between 0°C . and 300°C . For measurements at 0°C ., and at room temperatures, the quartz tube was immersed in a bath of ice and of water respectively. For observations at higher temperatures the tube was immersed in an iron bath, which contained

* *Loc. cit.*

† *Loc. cit.*

‡ Edwards, *loc. cit.*

substances boiling at different temperatures, and which was heated by a row of gas-jets placed underneath. In the present experiments, water, diethylaniline, eugenol, and diphenylamine boiling at approximately 100°C ., 215°C ., 256°C ., and 300°C . respectively were used in the heating-bath. By heating these substances to their boiling-points a steady temperature was reached, and accurate readings of the resistances could be taken, even at temperatures in the neighbourhood of 300°C . It was found that the temperatures of the boiling liquids generally increased slowly with long-continued heating; but this did not affect the accuracy with which measurements could be taken, as the change of temperature was negligible during the time required for a particular set of readings. Observations at each of these practically constant temperatures were continued over a long period, so that a large number of values of the resistance at a known temperature was obtained.

The temperature of the boiling liquid was measured by means of a platinum resistance thermometer previously calibrated, and a suitable mercury thermometer placed in the bath near the quartz capillary tube. The mercury thermometers were calibrated at the Reichsanstalt, and the high temperature and low temperature ones were divided into fifths and tenths of a degree centigrade respectively. The degree of accuracy attained in the measurement of the bath temperature is shown by the agreement between the temperatures indicated by the mercury and platinum thermometers in the neighbourhood of 300°C . The difference between them was never greater than 0.1°C . when the liquid was at its boiling-point.

EXPERIMENTAL DIFFICULTIES AND POSSIBLE ERRORS.

The chief difficulties encountered in the present investigation were: (i.) Thermoelectric currents; (ii.) formation of air-bubbles in the capillary, especially at high temperatures; and (iii.) variable contact resistance between the platinum wires fused through the glass leads and the amalgam contained in the quartz tube. Special precautions were taken to eliminate as far as possible errors due to the above causes.

The difficulty caused by thermoelectric currents was overcome by keeping the galvanometer circuit closed and adjusting the bridge resistance until there was no change in the continuous deflexion of the galvanometer on completing the battery circuit. Under these conditions, the value of the bridge resistance is equal to the resistance

to be measured in virtue of the properties of conjugate conductors.

The presence of air-bubbles could be detected quite easily during the experiments, as their effect was to increase the resistance of the amalgams, whereas the addition to the mercury of the metals employed in the preparation of the amalgams produced a decrease in the resistance. This difficulty was overcome by heating the quartz tube in a furnace to a temperature of about 315°C . and running all the amalgam into one of the vertical limbs of the tube, which was then closed by a stopper. Keeping the tube and contents still in the furnace, the amalgam was then allowed to run slowly through the capillary, and the rate of flow was regulated by the amount of air allowed to enter the limb through the stopper. By this means the bubbles were removed fairly quickly, but if, on examination with a lens, the presence of bubbles was still detected the process was repeated. Determinations of the resistance were then made, both at room and at high temperatures. After every high temperature reading, the presence of air-bubbles was again tested, both by means of a lens and also by re-determining the resistance of the column at room temperature. If this value was found to be the same as before, as was generally the case, it was assumed that no bubbles had been produced during the heating.

The possible errors introduced by variable contacts were found to be negligible in the case of mercury, but were appreciable in the case of the amalgams, especially those of the higher concentrations. The surface of the amalgam in each limb was generally covered with a thin film, probably caused by slight oxidation. Unless these films were cleanly pierced by the platinum points when the leads were introduced, the best contact was not obtained, and the resistance of the amalgam plus the leads was thus not correctly determined. This effect would not be serious if in the determination of the leads resistance the platinum points were similarly affected. Experience, however, showed that this was not the case, but the difficulty was largely overcome by removing as much of the film as possible, and by cleaning the platinum points with concentrated nitric acid before every determination.

It is estimated that the possible average error in the determination of $\frac{1}{C} \cdot \frac{\Delta L}{L}$ is not more than 10 per cent. for the lowest concentrations, and not more than 4 per cent.

for the highest concentrations. This corresponds to an average error in the resistance measurement of $\cdot 0001_{25}$ ohm.

METHOD OF CALCULATING THE RESISTIVITY AND CONDUCTIVITY OF THE AMALGAMS.

From the values obtained for the resistances of the column of mercury, and of amalgam, at a given temperature $t^{\circ}\text{C.}$, and the value of the resistivity of the former at the same temperature, the resistivity and conductivity of the amalgam at temperature $t^{\circ}\text{C.}$ were calculated as follows:—

Let R and R_{Am} be the resistances of the column of mercury and of amalgam respectively at temperature $t^{\circ}\text{C.}$; also let ρ and L be the values of the resistivity and conductivity respectively of mercury at temperature $t^{\circ}\text{C.}$, and ρ_{Am} and L_{Am} the corresponding values for the amalgam at the same temperature. If l and A denote the length and cross-section respectively of the column at the above temperature, then

$$\rho = R \left(\frac{A}{l} \right) \text{ and } \rho_{Am} = R_{Am} \left(\frac{A}{l} \right)$$

From these equations we obtain

$$\rho_{Am} = R_{Am} \left(\frac{\rho}{R} \right) \dots \dots \dots (1)$$

From (1), and the relation

$$L_{Am} = \frac{1}{\rho_{Am}} \dots \dots \dots (2)$$

the resistivity and conductivity of the amalgam at temperature $t^{\circ}\text{C.}$ can then be calculated in terms of the resistances of mercury and amalgam, and the resistivity of mercury at the same temperature.

If ΔL be the difference between L_{Am} and L at temperature $t^{\circ}\text{C.}$, and C the concentration of the amalgam expressed in gram atoms of metal dissolved in 100 gram atoms of mercury, then the value of $l \left(= \frac{1}{C} \cdot \frac{\Delta L}{L} \right)$ at temperature $t^{\circ}\text{C.}$ can be calculated. For this calculation the actual value of ΔL need not be obtained, for the value of $\frac{\Delta L}{L}$ can be found directly from the resistances thus:

$$\begin{aligned} \frac{\Delta L}{L} &= \frac{L_{Am} - L}{L} \\ &= \left(\frac{\rho}{\rho_{Am}} - 1 \right). \end{aligned}$$

Applying equation (1) we get

$$\frac{\Delta L}{L} = \left(\frac{R}{R_{Am}} - 1 \right). \quad . \quad . \quad . \quad (3)$$

Then

$$l = \frac{1}{C} \frac{\Delta L}{L}$$

$$= \frac{1}{C} \cdot \left(\frac{R - R_{Am}}{R_{Am}} \right). \quad . \quad . \quad . \quad (4)$$

This was the method actually employed in the present investigation for evaluating l .

EXPERIMENTAL RESULTS.

The Electrical Resistivity of Pure Mercury.

As previously explained, the method used in calculating the resistivity of an amalgam of known concentration involves measurements of the resistances of the mercury and the amalgam column under identical conditions. Such measurements in the case of mercury were carried out in the quartz tube, and the results are collected in Table I. Assuming the resistivity of mercury at 0° C. to

TABLE I.—Mercury.

Temperature, t° C.	Resistance in ohms, R_t .	Average temperature coefficient of resistance from 0° C. to t° C. (un- corrected for expansion of Quartz), $\times 10^4$.	Correction for expansion of Quartz, $= + \frac{R_t}{R_0} \cdot g$, $\times 10^4$.	Corrected average temperature coefficient of resistance (and resis- tivity) from 0° C. to t° C., $\times 10^4$.	Resistivity of Mercury at t° C. $\times 10^8$.	Con- ductivity of Mercury at t° C.
0.0	.3333 ₄	—	—	—	9407 ₄	10629 ₉
11.5	.3367 ₈	8.974	.005	8.979	9504 ₇	10521 ₁
100.0	.3362 ₃	9.867	.005	9.872	10336 ₁	9674 ₈
217.3	.4136 ₂	11.083	.006	11.089	11674 ₂	8565 ₈
257.5	.4321 ₇	11.514	.006	11.520	12197 ₅	8198 ₄
300.0	.4530 ₄	11.970	.007	11.977	12787 ₆	7820 ₁

be 94074×10^{-9} , and correcting for the expansion of the quartz envelope, the resistivities of mercury at various temperatures can be calculated. The results obtained agree within the limits of experimental error with values obtained by Edwards *, who found that,

$$\rho_t = 94074 \times 10^{-9} [1 + 0.8877t + 0.977t^2 + 0.19t^3].$$

The Electrical Conductivity of dilute Gold Amalgams.

So far as the author is aware, no previous determinations of the conductivity of dilute gold amalgams have been made. Determinations, however, have been made of the conductivity of gold amalgams whose concentrations were much greater than those employed in this investigation. Matthiesen and Vogt † measured the conductivity of amalgams containing between 80 per cent. and 90 per cent. of gold, whilst Parravano and Jovanovich ‡ made observations with amalgams containing about 60 per cent. of gold. In both cases the conductivity was found to increase with increase in the concentration of gold dissolved in mercury. However, owing to the great difference in the concentrations, the results for the above amalgams are not comparable with those obtained in the present experiments.

The gold employed in the present investigation was very pure, and was obtained in the form of thin foil from Johnson, Matthey & Co., London. The amalgams were prepared by the direct addition of the gold to the mercury. It was found that the gold goes into solution only very slowly at ordinary room temperatures, but much more rapidly if the mercury is heated beforehand.

Determinations of resistivity were made for nine different amalgams having concentrations varying between .04 per cent. and .32 per cent. by weight of gold in mercury. According to Gouy §, the solubility of gold in mercury at room temperatures is .13 per cent. by weight. In the present work, however, it was found possible to prepare, and also to make determinations with amalgams containing even .32 per cent. of gold at room temperatures. This also represents the limit of solubility, for, any further addition of gold produced no change in the resistance of the amalgam column, and the excess of gold remained out of solution.

* *Loc. cit.*

† Matthiesen and Vogt, *Pogg. Ann.* cxvi. p. 376 (1862).

‡ Parravano and Jovanovich, *Gazz. Chim. Ital.* xlix. (i.), p. 1 (1919).

§ A. Gouy, *Journ. Phys.* (3) iv. p. 320 (1895).

The amalgams were contained in the same quartz tube as that used for the mercury determinations, and the resistance determined at the following temperatures:—11·5° C., 100° C., and 300° C. For two amalgams of concentration ·12 per cent. and ·24 per cent., the resistance was further determined at 217·3° C. and 257·5° C.; thus enabling the average temperature coefficient of resistivity of the amalgam to be calculated at various stages of temperature between 11·5° C. and 300° C.

TABLE II.—Gold Amalgams.

Percentage weight of Gold in Mercury.	Concentration "C."	Resistance in ohms of column at temperature t° C.				
		$R_{11\cdot5^{\circ}}$	$R_{100^{\circ}}$	$R_{217\cdot3^{\circ}}$	$R_{257\cdot5^{\circ}}$	$R_{300^{\circ}}$
0 (Mercury).		·3367 ₈	·3662 ₃	·4136 ₂	·4321 ₇	·4530 ₄
·04004	·0407	·3362 ₄	·3654 ₀	—	—	·4514 ₈
·06006	·0611	·3359 ₄	·3649 ₈	—	—	·4507 ₀
·08001	·0814	·3357 ₀	·3645 ₀	—	—	·4500 ₅
·12000	·1221	·3350 ₄	·3636 ₈	·4101 ₇	4282 ₇	·4487 ₂
·16015	·1629	·3344 ₇	·3629 ₃	—	—	·4475 ₉
·20020	·2036 ₆	·3340 ₁	·3620 ₃	—	—	·4464 ₅
·24001	·2441	·3333 ₁	·3613 ₁	·4072 ₇	·4254 ₁	·4456 ₈
·28002	·2348	·3328 ₅	·3606 ₈	—	—	·4448 ₇
·32000	·3255	·3324 ₀	·3601 ₀	—	—	·4442 ₃

The resistances obtained for the column of amalgams of various concentrations are given in Table II., and their relative values are shown in Graph I. Table III. gives the corresponding values obtained for the resistivities and conductivities of the amalgams. The average temperature coefficient of resistivity of an amalgam of percentage weight ·12 (or "C"=·1221) for various temperature intervals between 11·5° C. and 300° C. as determined from the observed resistances, is given in Table IV., and the values of this coefficient between 11·5° C. and 100° C., for amalgams of various concentrations are collected in Table V.

TABLE III.—Gold Amalgam.

Temperature, t° C.	Percentage weight of Gold in Mercury.	Concen- tration “C.”	Resistivity of Pure Mercury at t° C., × 10 ⁸ .	Conduc- tivity of Pure Mercury at t° C.	Resistivity of Amalgam at t° C., × 10 ⁸ .	Conduc- tivity of Amalgam at t° C.
11.5	·04004	·0407	9505	10521	9490	10538
	·06006	·0611	”	”	9481	10547
	·08001	·0814	”	”	9475	10555
	·12000	·1221	”	”	9456	10576
	·16015	·1629	”	”	9440	10594
	·20020	·2036 ₅	”	”	9427	10608
	·24001	·2441	”	”	9407	10631
	·28002	·2848	”	”	9394	10645
	·32000	·3255	”	”	9381	10660
100	·04004	·0407	10336	9675	10313	9697
	·06006	·0611	”	”	10301	9708
	·08001	·0814	”	”	10287	9721
	·12000	·1221	”	”	10264	9743
	·16015	·1629	”	”	10243	9763
	·20020	·2036 ₅	”	”	10217	9787
	·24001	·2441	”	”	10197	9807
	·28002	·2848	”	”	10179	9824
	·32000	·3255	”	”	10163	9840
217.3	·12000	·1221	11674	8566	11577	8638
	·24001	·2441	”	”	11495	8700
257.5	·12000	·1221	12197.5	8198	12087	8273
	·24001	·2441	”	”	12007	8329
300	·04004	·0407	12788	7820	12743	7847
	·06006	·0611	”	”	12722	7860
	·08001	·0814	”	”	12704	7872
	·12000	·1221	”	”	12666	7895
	·16015	·1629	”	”	12634	7915
	·20020	·2036 ₅	”	”	12602	7935
	·24001	·2441	”	”	12580	7949
	·28002	·2848	”	”	12557	7963.5
	·32000	·3255	”	”	12539	7975

The variation of this coefficient with the concentration can be seen from Graph II. For purposes of comparison, the

TABLE IV.—Gold Amalgams.
Amalgam of Concentration "C" = .1221.

Temperature, $t^{\circ}\text{C.}$	Resistivity of Mercury at $t^{\circ}\text{C.}$, $\times 10^8$.	Resistivity of Amalgam at $t^{\circ}\text{C.}$, $\times 10^8$.	Average temperature coefficient of resistivity of Mercury from 11.5°C. to $t^{\circ}\text{C.}$, $\times 10^4$.	Average temperature coefficient of resistivity of Amalgam from 11.5°C. to $t^{\circ}\text{C.}$, $\times 10^4$.	$\frac{\Delta L}{L} \times 10^2$.
11.5	9505	94.6	—	—	.519
100.0	10336	10264	9.886	9.664	.701
217.3	11674	11577	11.093	10.902	.841
257.5	12197.5	12087	11.520	11.318	.911
300.0	12788	12666	11.973	11.768	.963

TABLE V.—Gold Amalgams.

Concentration "C."	Average tem- perature coefficient of resistivity of Amalgams from 11.5°C. to 100°C. , $\times 10^4$.	Concentration "C."	Average tem- perature coefficient of resistivity of Amalgams from 11.5°C. to 100°C. , $\times 10^4$.
0 (Mercury).	9.886	.1629	9.610
.0407	9.804	.2036 ₅	9.484
.0611	9.773	.2441	9.497
.0814	9.699	.2848	9.452
.1221	9.664	.3255	9.421

values of $\frac{\Delta L}{L}$, $\frac{1}{C} \frac{\Delta L}{L} (=l)$, l_{∞} , and $(l_{\infty} - l)$ are included together with the corresponding values for copper amalgams

in Table IX. and the variations of $\frac{\Delta L}{L}$, l , and $(l_{\infty} - l)$, with changes in concentration can be seen from Graphs III., IV., and V. respectively.

The Electrical Conductivity of dilute Copper Amalgams.

As in the case of the gold amalgams, very little work has been done on the conductivities of dilute amalgams of copper, and the only investigation dealing with concentrations comparable with those used in the present experiments is that due to Johns and Evans*. The conductivities of very concentrated amalgams, however, were determined by Batelli†, Schleicher‡, and Michaelis§; but, on account of the large difference in the respective ranges of concentrations, their results cannot be compared with those obtained in the present work. The results of Johns and Evans||, on the other hand, were obtained for amalgams containing respectively .01 per cent., .015 per cent., and .02 per cent., by weight of copper, and their determinations were all made at 300° C. Their observations, covering only a small range of concentrations, were, however, rather irregular.

In the present investigation, determinations of the conductivities were made at 11.5° C., 100° C., as well as at 300° C., and the measurements were carried out over a greater range of concentrations than those studied by Johns and Evans. In fact, at each temperature, determinations were made for increasing concentrations up to the limit of solubility of copper in mercury. Different values are given by different workers for the solubility of copper in mercury. This is undoubtedly due to the difficulty in getting the copper into solution, and depends to a great extent on the method by which the amalgam is prepared. In the present work the amalgam was prepared by direct addition of the finest electrolytic copper to mercury. The copper had previously been cleaned with dilute sulphuric acid, washed with distilled water, dried, and then reduced to very fine filings. Even when the mercury was heated to about 300° C., the copper was found to be only sparingly soluble in it.

* *Loc. cit.*

† *Loc. cit.*

‡ Schleicher, *Zeit. Electrochem.*, xviii. p. 998 (1912).

§ Michaelis, *Dissert.* Berlin (1883).

|| *Loc. cit.*

The conductivities of seven different amalgams, of concentrations ranging between .010 per cent. and .044 per cent. by weight, were determined at 300° C. It was found impossible to prepare amalgams containing more than .01 per cent. of copper at room temperatures, and more than .015 per cent. of copper at 100° C., for any further addition of copper was found to produce no change in the resistance, and the excess of copper remained out of solution.

The observed values of the resistances of the amalgam column of various concentrations are given in Table VI. and

TABLE VI.—Copper Amalgams.

Percentage weight of Copper in Mercury.	Concentration "C."	Resistance in ohms of column at temperature $t^{\circ}\text{C}$.		
		$R_{115^{\circ}}$.	$R_{100^{\circ}}$.	$R_{300^{\circ}}$.
0 (Mercury).		.3367 ₈	.3362 ₃	.4530 ₄
.01020	.0122	.3363 ₅	.3655 ₈	.4517 ₉
.01531	.0183	—	.3652 ₃	.4512 ₀
.02042	.0643	—	—	.4506 ₅
.02540	.0802	—	—	.4501 ₉
.03137	.0990	—	—	.4495 ₉
.03516	.1110	—	—	.4492 ₃
.04437	.1406	—	—	.4485 ₃

the corresponding values of the resistivities and conductivities in Table VII. Table VIII. gives the comparison between the values of the temperature coefficient of resistivity, and the resistivity of mercury with the corresponding values obtained for an amalgam containing .01 per cent. by weight

("C"=.0322) of copper. The values obtained for $\frac{\Delta L}{L}$, l ,

l_{∞} , and $(l_{\infty} - l)$ are shown in Table IX., and the variations of these values, with concentration, are shown in Graphs III., IV., and V.

TABLE VII.—Copper Amalgams.

Temperature, $t^{\circ}\text{C.}$	Per- centage weight of Copper in Mercury.	Con- centration “C.”	Resistivity of Pure Mercury at $t^{\circ}\text{C.}$, $\times 10^8$.	Con- ductivity of Pure Mercury at $t^{\circ}\text{C.}$	Resistivity of Amalgam at $t^{\circ}\text{C.}$, $\times 10^8$.	Con- ductivity of Amalgam at $t^{\circ}\text{C.}$
11.5	·01020	·0322	9505	10521	9493	10534
100.0	·01020	·0322	10336	9675	10318	9692
	·01531	·0483	„	„	10308	9701
300.0	·01020	·0322	12788	7820	12753	7841
	·01531	·0483	„	„	12736	7852
	·02042	·0643	„	„	12721	7861
	·02540	·0802	„	„	12708	7869
	·03137	·0990	„	„	12691	7880
	·03516	·1110	„	„	12680	7886
	·04437	·1406	„	„	12661	7898

TABLE VIII.—Copper Amalgam.

Amalgam of Concentration “C” = ·0322.

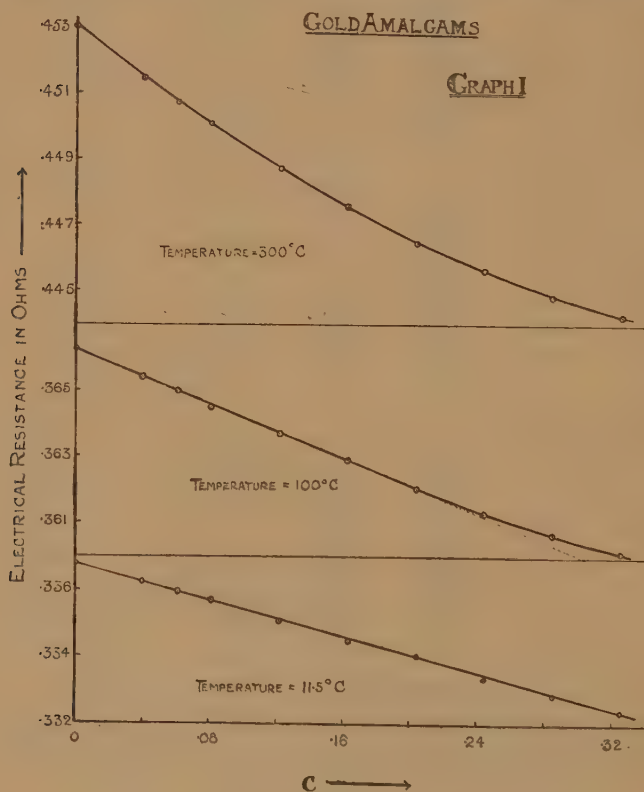
Tem- perature, $t^{\circ}\text{C.}$	Resistivity of Pure Mercury at $t^{\circ}\text{C.}$, $\times 10^8$.	Resistivity of Amalgam at $t^{\circ}\text{C.}$, $\times 10^8$.	Average temperature coefficient of resistivity of Mercury from 11.5°C. to $t^{\circ}\text{C.}$, $\times 10^4$.	Average temperature coefficient of resistivity of Amalgam from 11.5°C. to $t^{\circ}\text{C.}$, $\times 10^4$.	$\frac{\Delta L}{L} \times 10^2$.
11.5	9505	9493	—	—	·128
100.0	10336	10318	9.886	9.828	·178
300.0	12788	12753	11.973	11.903	·277

TABLE IX.

Nature of Amalgam.	Temperature ° C.	Concentration " C."	$\frac{\Delta L}{L} \times 10^2.$	$\frac{1}{C} \cdot \frac{\Delta L}{L} (=l) \times 10^2.$	$l_{\infty} \times 10^2.$	$(l_{\infty} - l) \times 10^2.$
Gold.	11.5	.0407	.161	3.95	4.1	
	"	.0611	.250	4.09		
	"	.0814	.322	3.95		
	"	.1221	.519	4.25		
	"	.1629	.691	4.24		
	"	.2036 ₅	.829	4.07		
	"	.2441	1.041	4.27		
	"	.2848	1.181	4.15		
	"	.3255	1.318	4.05		
Gold.	100.0	.0407	.228	5.60	5.6	
	"	.0611	.343	5.61		
	"	.0814	.475	5.83		
	"	.1221	.701	5.74		
	"	.1629	.909	5.58		
	"	.2036 ₆	1.160	5.70		
	"	.2441	1.362	5.58		
	"	.2848	1.539	5.40		
	"	.3255	1.702	5.23		
Gold.	300.0	.0407	.350	8.60	9.0	.40
	"	.0611	.519	8.50		.50
	"	.0814	.664	8.16		.84
	"	.1221	.963	7.88		1.12
	"	.1629	1.218	7.48		1.52
	"	.2036 ₅	1.476	7.25		1.75
	"	.2441	1.651	6.76		2.24
	"	.2848	1.836	6.45		2.55
	"	.3255	1.983	6.09		2.91
Copper.	11.5	.0322	.128	3.97	4.0	
Copper.	100.0	.0322	.178	5.52	5.6	
	"	.0483	.274	5.67		
Copper.	300.0	.0322	.277	8.59	9.0	.41
	"	.0483	.408	8.44		.56
	"	.0643	.530	8.25		.75
	"	.0802	.633	7.89		1.11
	"	.0990	.768	7.75		1.25
	"	.1110	.848	7.64		1.36
	"	.1406	1.006	7.15		1.85

DISCUSSION OF RESULTS.

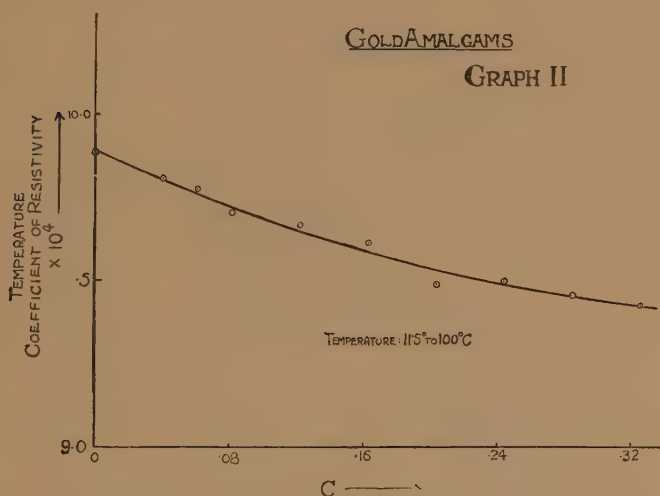
It can be seen from Tables II. and VI. that the resistance of mercury is decreased by the addition of gold or copper, and that this change becomes greater with increase in temperature. From Graph I. for gold amalgams, it is observed that at 11.5°C . the resistance of the amalgams is a linear function of the concentration; whereas at 100°C .



and 300°C . there is a deviation from the linear law, and this deviation is seen to be more rapid at the higher temperature. This is also the case with the copper amalgams.

Correspondingly, as shown in Tables III. and VII., there is an increase in the conductivity of the amalgam with concentration, and this change of conductivity as compared with mercury increases with increase in temperature, when the concentration of the amalgam is small.

From Tables IV. and VIII. it can be seen that both for a gold amalgam of concentration " C " = .1221, and for a copper amalgam of concentration " C " = .0322, the average temperature coefficient of resistivity of the amalgam between 11.5°C . and the various higher temperatures increases with increase in temperature-difference. However, the values in each case are seen to be less than the corresponding values obtained for mercury. In addition, it is clearly shown in Table V. and Graph II., that for the gold amalgams, the difference between the average temperature-coefficient of resistivity of the amalgam and that of mercury between 11.5° and 100°C . becomes greater as the concentration of the amalgam is increased.

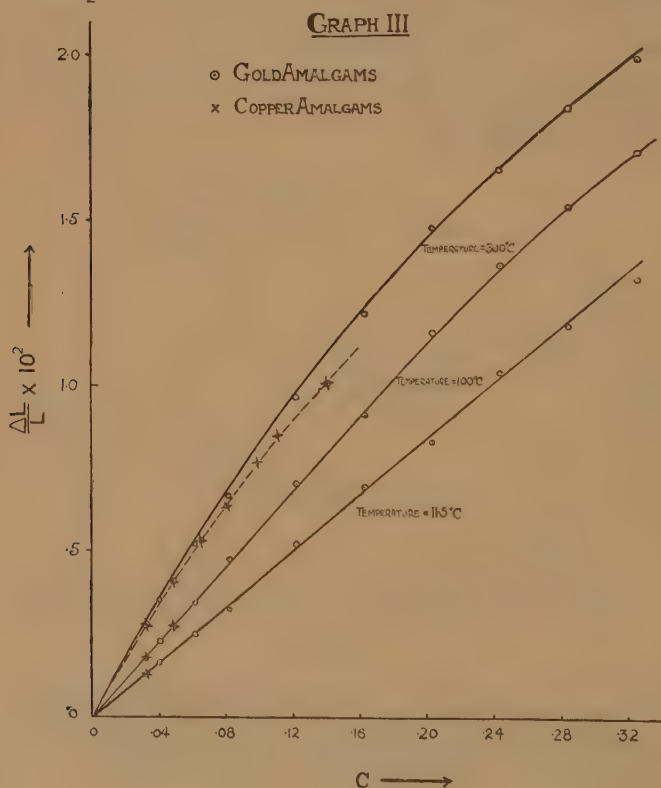


The values obtained for the quantities necessary to discuss the results for copper and gold amalgams in relation to Skaupy's theory*, have been collected in Table IX. The concentration " C " is expressed in gram atoms of metal per

100 gram atoms of mercury; and $\frac{\Delta L}{L}$ is the increase in conductivity relative to that of mercury at the same temperature. The sixth column gives the value of l for infinite dilution, *i. e.*, the value of the ratio of the increase of conductivity relative to mercury at the same temperature, to the concentration, when the latter is very small.

* *Loc. cit.*

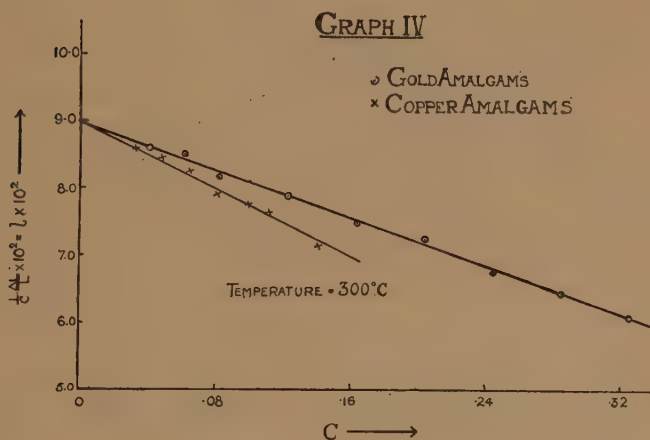
It can be seen from column 4, Table IX., and also from Graph III., that the value of $\frac{\Delta L}{L}$ increases both with increase in concentration and with increase in temperature for gold and copper amalgams. At room temperatures the relation between $\frac{\Delta L}{L}$ and "C" is linear, but at high temperatures



the relation deviates from the linear law. The values obtained for copper amalgams have been plotted in Graph III. for comparison with those obtained for the gold amalgams. However, owing to the impossibility of preparing more concentrated amalgams at 11.5° C. and 100° C., an extended set of curves for copper amalgams analogous to those obtained for gold amalgams cannot be obtained, and a complete comparison of the respective values of $\frac{\Delta L}{L}$ at the lower

temperatures cannot be made. At the lower concentrations the corresponding values of $\frac{\Delta L}{L}$ are practically the same for both amalgams, but at higher concentrations at a temperature of 300° C. there is a marked difference between them, the copper amalgams having the smaller values. This shows that the effect of copper and gold on the conductivity of mercury is practically the same for small concentrations; but, with increase in concentration, the effect of copper is less than that of gold, especially at high temperatures.

The values of $l \left(= \frac{1}{C} \frac{\Delta L}{L} \right)$ are given in column 5, Table IX.,



and its variation with concentration "C" at 300° C. is shown in Graph IV. The relation in both cases (copper and gold) is a linear one, sloping downwards towards the axis of concentration. The value of l_{∞} is the value of l at the point where the straight line graph meets the axis of l . This value was found to be 9.0×10^{-2} both for copper and for gold amalgams. It is not in agreement with the value obtained by Johns and Evans* for copper amalgams. In their experiments, however, they only considered three low concentrations, and the values they obtained for l varied irregularly with concentration. They took l_{∞} to be the mean of these three values of l , and in this way found its value to

* *Loc. cit.*

be 6.5×10^{-2} . The disagreement between these two values of l_{∞} for copper amalgams is probably due to the experimental difficulties met with in dealing with this amalgam, namely, the low concentrations possible, the liability of its surface to oxidize, and the slowness with which the copper goes into solution. Any consequent errors would have a serious effect on the value of l for low concentrations, such as those considered by Johns and Evans. By increasing the concentration, however, the effect of errors of observation on the value of l would be greatly diminished. This was done in the present experiments, and the results obtained for copper amalgams of different concentrations are in better agreement amongst themselves than those obtained by Johns and Evans*, and clearly indicate that their values were too low. The lower values of l obtained by them may possibly be due to their having taken insufficient precautions to ensure that the copper was completely dissolved.

At 11.5° C. and 100° C. for gold amalgams the values of l were found to be practically constant for all concentrations, and l_{∞} was taken to be the mean value. In this way it was found that l_{∞} was 4.1×10^{-2} at 11.5° C., and 5.6×10^{-2} at 100° C. For copper amalgams only one value of l was obtained at 11.5° C., and this was taken to be the value of l_{∞} . Even at 100° C. only two values of l were obtained, and in this case l_{∞} was taken to be the mean of both. In this way it was found that l_{∞} for copper amalgams was 4.0×10^{-2} at 11.5° C., and 5.6×10^{-2} at 100° C.

It can therefore be taken that the corresponding values of l_{∞} are the same within experimental error for both the copper and the gold amalgams.

Johns and Evans* in their work also made a thorough investigation of the change produced in the conductivity of mercury by the addition of silver; and it is interesting to note that the values they obtained for l_{∞} for silver amalgams agree, within experimental error, with those obtained in the present work for copper and gold amalgams. The comparison can be made from the values collected in Table X.

According to Skaupy's theory†, which has been referred to previously, the value of $(l_{\infty} + r_{\infty})$ should be of the same order of magnitude for different metals dissolved in mercury. Unfortunately, the values of r_{∞} at 11.5° , 100° , and 300° C. are not known for amalgams of concentrations equal to those employed in the present experiments, and, therefore, one is

* *Loc. cit.*

† *Loc. cit.*

obliged to consider the values of l_{∞} alone in relation to the different amalgams. As we have already seen from the values obtained by the present authors for copper and gold amalgams, and those obtained by Johns and Evans for silver amalgams (as seen in Table X.), it can be concluded that the value of l_{∞} , at the same temperature, is the same, within experimental error, for amalgams of all the metals in Group 1 (b) in the Periodic Table. This means that, atom for atom, the effect of copper, silver, and gold on the conductivity of mercury is the same, provided the concentration is small.

A further point in Skaupy's* theory is that, neglecting the variation of viscosity with concentration, the value of $\left(\frac{l_{\infty}-l}{C}\right)$ should be constant. At 11.5° C. and 100° C. there

TABLE X.

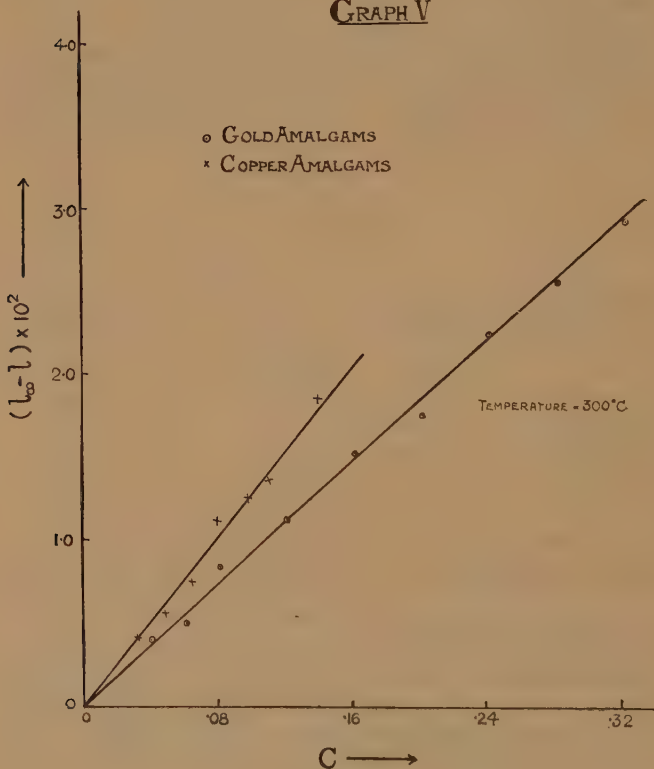
Temperature ° C.	$l_{\infty} \times 10^2$ for Copper.	$l_{\infty} \times 10^2$ for Silver.	$l_{\infty} \times 10^2$ for Gold.
11.5	4.0	4.0 (at 15° C.)	4.1
100.0	5.6	5.3	5.6
300.0	9.0	9.0	9.0

was very little change in the value of l with concentration, and, consequently, the values of $\left(\frac{l_{\infty}-l}{C}\right)$ at those temperatures are not discussed. However, at 300° C., as seen in Table IX., the value of $(l_{\infty}-l)$ increased with concentration in the case of both copper and gold amalgams. The variation of $(l_{\infty}-l)$ with "C" is shown in Graph V., and the relation between the two quantities is approximately a linear one, thus showing that $\left(\frac{l_{\infty}-l}{C}\right)$ is approximately constant. It is important to point out here that an accurate experimental determination of l is very difficult for low concentrations and that any error in its value involves a much greater percentage error in the value of $(l-l_{\infty})$.

* *Loc. cit.*

A possible explanation of the increase in the value of $l \left(= \frac{1}{C} \frac{\Delta L}{L} \right)$ with temperature is that the electron concentration in the amalgam as compared with mercury is increased with increase of temperature; but the question of whether viscosity enters into the problem in any form.

GRAPH V



must be left until experiments have been carried out on alkali amalgams.

SUMMARY.

1. The conductivities of dilute amalgams of copper and gold have been determined at 11.5° , 100° , and 300°C . In the case of gold amalgams, at each temperature the conductivity was determined over a range of concentrations equal

to the maximum range possible at $11.5^{\circ}\text{C}.$; whilst for copper amalgams, at each temperature the determinations were made for increasing concentrations up to the limit of solubility of copper in mercury at that temperature. For gold amalgams of concentrations " C " = $.1221$ and " C " = $.2441$, the conductivity was also measured at 217.3° and $257.5^{\circ}\text{C}.$

2. The average temperature coefficients of resistivity between 11.5° and $t^{\circ}\text{C}.$ of gold amalgam of concentration " C " = $.1221$, and of copper amalgam of concentration " C " = $.0322$, were measured, and in both cases were found to increase as the temperature difference increased. However, the values were less than the corresponding ones in the case of pure mercury.

3. The values of the average temperature coefficients of resistivity of gold amalgams of various concentrations, between 11.5° and $100^{\circ}\text{C}.$, showed a diminution as the concentration increased.

4. In the case of gold amalgams, at 11.5° and $100^{\circ}\text{C}.$ the increase of conductivity relative to the conductivity of mercury at the same temperature was practically proportional to the concentration, but at $300^{\circ}\text{C}.$, in the case of both copper and gold amalgams, this was found not to be the case.

5. For copper and gold amalgams, the value of $\frac{1}{C} \cdot \frac{\Delta L}{L}$ (*i. e.*, the ratio of the increase of conductivity relative to mercury to the concentration) was determined at each temperature and for each concentration, and the values compared with the corresponding ones obtained by Johns and Evans* for silver amalgams. It was found that the value of $\frac{1}{C} \cdot \frac{\Delta L}{L}$ at infinite dilution (*i. e.*, for extremely small concentrations) was practically the same at the same temperature for amalgams of copper, silver, and gold. This means that, atom for atom, the effect on the conductivity of mercury of the different metals in Group I. (b) in the Periodic Table is the same.

October 1st, 1928.

* *Loc. cit.*

CXXI. *Electronic Waves and the Electron.* By Sir J. J. THOMSON, O.M., F.R.S., Master of Trinity College, Cambridge*.

SUMMARY.

RECENT experiments have shown that a moving electron is accompanied by a train of waves. No such waves would be produced by the motion of an electron if, as hitherto assumed, it consisted solely of a point charge of electricity. The electric and magnetic forces round a moving electron of this type can be calculated from Maxwell's equations and have long been known, and there is nothing in the distribution of these forces approaching that in a train of waves. In this paper it is shown that if the structure of the electron were such that this point charge or something analogous to it formed a nucleus which was surrounded by a system such as we shall proceed to describe, then the motion of the electron would from the ordinary laws of electro-dynamics give rise to a train of waves, and, moreover, that the relation between the wave-length of this train and the velocity of the electron is exactly that indicated by the experiments of G. P. Thomson. The electronic waves on this view are electrical waves, but they do not travel through the normal ether, but through an ether modified by the system which envelops the nucleus of the electron. These waves would be produced if the system enveloping the nucleus, and which we shall call the "sphere" of the electron, were made up of parts which can be set in motion by electric forces, and when in motion produce the effects of electric currents. Such a structure might consist either of a distribution of discrete lines of force, or of a number of positively- and negatively-electrified particles distributed through the sphere of the electron. These would behave like free particles, even though the opposite charges were bound together in doublets, if the frequency of the forces acting upon them were large compared with the natural frequencies of the doublets. The properties of a structure of this kind are discussed, and it is shown that the sphere of the electron would have a definite period of vibration, the frequency of the vibration being proportional to the square root of the number of electrified systems per unit volume. These vibrations are of a peculiarly interesting kind, inasmuch as though they are electrical vibrations they are not accompanied by any radiation of energy, so that when once started

* Communicated by the Author.

they are maintained for an indefinite time. The vibrations consist of an oscillating electric field which is not accompanied by a magnetic one, the Poynting vector vanishes, and there is no transmission of energy. The sphere of the electron can thus vibrate, and so also can the nucleus, the time of vibration for the nucleus being proportional to the time light takes to travel round its circumference. Thus the two parts of the electron, the nucleus and the sphere, are each capable of vibration, and when the electron is in a steady state the vibrations of the two parts will be in resonance. The electron has thus, in addition to the steady electric field due to the negative charge on the nucleus, an alternating field in which the energy remains constant since there is no radiation. The oscillating field is the seat of energy, and thus the total energy of the electron is that due to the charge on the nucleus plus that due to the oscillating field. This is important in connexion with the calculation of the size of the electron. The usual estimate 1.4×10^{-13} cm. for the radius, a , is deduced on the assumption that the energy due to the charge on the nucleus $e^2/2a$ accounts for the whole of the energy of the electron; if $e^2/2a$ represents but a part, and it may be a small part, of the total energy, the corresponding value of a would be much larger.

Stationary Electron.

When the nucleus is not in motion it is shown that the components of the oscillating electric and magnetic forces are represented by equations of the form

$$\cos p_0 t \cdot f(x, y, z), \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

where p_0 is the period of vibration of the electron and f a function such that

$$\frac{d^2 f}{dx^2} + \frac{d^2 f}{dy^2} + \frac{d^2 f}{dz^2} = 0.$$

An interesting special case representing a symmetrical electron is when

$$X = A \cos p_0 t \cdot \frac{d}{dx} \frac{1}{r}, \quad Y = A \cos p_0 t \cdot \frac{d}{dy} \frac{1}{r}, \quad Z = A \cos p_0 t \cdot \frac{d}{dz} \frac{1}{r};$$

$$\alpha = \beta = \gamma = 0.$$

(X, Y, Z) (α, β, γ) are the components of the electric and magnetic forces respectively and r the distance from the centre of the nucleus. Here the oscillating electric force is radial and always proportional to the steady force due to the

charge on the nucleus. The energy per unit volume due to the oscillating field and that due to the steady field bear a constant ratio to each other. It should be noticed that the total energy due to the oscillations remains constant, although the electric forces vanish periodically, for this energy is made up of two parts—one due to the electric field itself, the other to the kinetic energy of the moving electrified particles in the sphere; the sum of these two parts is constant. Since in each unit of volume the energy due to the oscillating field bears a constant ratio to that due to the field of the nucleus, the total energy of this field in the electronic sphere will be proportional to that of the nucleus, *i. e.* to $e^2/2a$, the total energy of the electron which is the sum of these parts will also be proportional to $1/a$. The time of vibration of the electron is proportional to the time light takes to travel round the circumference of the nucleus, and thus the frequency is proportional to $1/a$. The ratio of the energy of the electron to the frequency of its vibrations is thus independent of the size of the nucleus—this ratio is Planck's constant for the electron. Reasons are given for thinking that when an electron of this type emits *light* the energy in the quantum of the light it emits will bear to the frequency of the light the same ratio as the energy of the electron bears to the frequency of its vibrations. Thus Planck's law would be a consequence of the structure of the electron.

The Electron in Motion.

By using Maxwell's equations we find that when an electron of this type moves parallel to the axis of x with uniform velocity u , the field is given by the equations

$$Y = A' \cos p \left(t - \frac{ux}{c^2} \right) \cdot \frac{d}{dy} \frac{1}{R}, \quad Z = A' \cos p \left(t - \frac{ux}{c^2} \right) \cdot \frac{d}{dz} \frac{1}{R},$$

$$\alpha = 0, \quad \beta = -uA' \cos p \left(t - \frac{ux}{c^2} \right) \cdot \frac{d}{dz} \frac{1}{R},$$

$$\gamma = uA' \cos p \left(t - \frac{ux}{c^2} \right) \cdot \frac{d}{dy} \frac{1}{R},$$

where

$$R^2 = k^2(x - ut)^2 + y^2 + z^2, \quad p = p_0 k,$$

$$k^2 = \frac{1}{1 - \frac{u^2}{c^2}}.$$

Thus the field consists of plane waves of electric and magnetic force of diminishing amplitude travelling along the direction of motion of the electron. The wave-length λ of the waves is given by the equation

$$\lambda = 2\pi c^2 \sqrt{1 - \frac{u^2}{c^2}} / p_0 u ; \dots \dots \dots \text{(II.)}$$

thus λu is proportional to $\sqrt{1 - \frac{u^2}{c^2}}$. This is precisely the

relation found by G. P. Thomson in his experiments on the diffraction of electrons. This expression for the wave-length is not confined to any particular distribution of the alternating field in the electron at rest. In the most general case, where one of the components of electric force in the electron at rest is given by an expression of the form $\cos p_0 t \cdot f(x, y, z)$, it can be shown that for the moving electron the solution is $\cos p \left(t - \frac{ux}{c^2} \right) f(k(x - ut), y, z)$, giving

waves of the same length as the special solution we considered. Thus it follows from the principles of classical electrodynamics that a moving electron of the type we are discussing will be accompanied by a train of waves; the electronic waves on this view are waves of electric and magnetic force differing from plane waves passing through the normal ether in that the magnetic force in the electronic waves is, relatively to the electric force, smaller than in the normal electric waves.

The electronic waves and the electron must always move in the same direction. Hence, if the direction of the electronic waves is deflected, as in the experiments on diffraction, the path of the electron will be bent; conversely, if the path of the nucleus is changed by the action of applied forces on its charge, the path of the waves will be changed also.

The periods and properties of the electronic waves afford some evidence as to the sizes both of the nucleus and the sphere which surrounds it. The wave-length of waves associated with electrons moving with known speed have been determined by G. P. Thomson. From these values we find from equation (II.) that p_0 is about 1.1×10^{20} . Since the vibrations of the sphere and the nucleus are in resonance, this will also be the frequency of the vibrations of the nucleus. The time of these vibrations will be comparable with the time light takes to travel over the circumference of the nucleus, so that the frequency will be of the order $c/2\pi a$;

comparing this with the value 1.1×10^{20} , we find that a must be of the order 5×10^{-11} , which is very much larger than the value 1.4×10^{-13} deduced from the hypothesis that the electron consists of the nucleus alone.

Size of the "Sphere" round the Electron.

The electronic waves must be in a super-dispersive medium, *i. e.* in the sphere, hence the length of the train of these waves will be a guide to the diameter of the sphere. G. P. Thomson, from his experiments on diffraction, estimates the length of the train as at least 5×10^{-8} cm., which indicates that the size of the sphere is large compared with an atom. It is possible, however, that though there must be a super-dispersive medium of at least this length, the whole of that medium need not consist of the sphere of the moving electron. For if the sphere of an electron is even as large as an atom, then in a solid the spheres of the electrons in the closely-packed molecules will overlap, so that an electron travelling through it would be surrounded by a super-dispersive medium as large as the solid itself. The moving electron will excite in this medium waves whose length is the same as that of the electronic waves given by equation (II.); hence the length of the train will be fixed by the dimensions of the solid, and not by that of the sphere of a single electron. This would not apply unless the size of this sphere were comparable with the size of an atom, and therefore large compared with the nucleus, even if we adopt the new instead of the old estimate of the size of the latter.

Field Equations inside an Atom.

If the sphere of the electrons is comparable in size with the atom, the region inside an atom containing several electrons will be a super-dispersive region, and the field equations for the components of the electric and magnetic forces will be of the type

$$c^2 \left(\frac{d^2 \psi}{dx^2} + \frac{d^2 \psi}{dy^2} + \frac{d^2 \psi}{dz^2} \right) = \frac{d^2 \psi}{dt^2} + p_0^2 \psi. \quad (\text{III.})$$

It must be remembered that the sphere of the electron only comes into evidence when it is exposed to exceedingly rapid vibrations; when the frequency of the vibration is small compared with p_0 , the sphere behaves like the normal ether.

In a solid where the molecules are tightly packed the spheres of their electrons might overlap and fill the solid with a super-dispersive medium in which the field equations

would be of the type (III.). If an electrical wave, of frequency p , whether accompanied by an electron or not passed through the solid, the refractive index would be $\sqrt{p^2 - p_0^2}/p$; hence if p were greater than p_0 but comparable with it, the properties of the wave would vary rapidly with the value of p , and there would also be great differences between the properties of waves whose frequency was considerably less than p_0 and those whose frequencies were greater, though not infinitely greater. Now, among the γ -rays from radium C there are some whose frequencies are greater than p_0 (1.1×10^{20}), others whose frequencies are much smaller, so that if we could isolate these rays the point under discussion could be subject to a very direct test. It is very difficult, however, to get anything like a monochromatic beam of γ -rays. I tried an experiment of another kind, testing whether or not the harder γ -rays were, like electrons, deflected by an electric force. Since the nucleus of the electron and the electronic waves always travel in the same direction, the deflexion of the electron by electric force might be due to either to the deflexion of the waves or the deflexion of the nucleus. The waves would be deflected if the electric force produced a gradient in the refractive index of the medium through which they travel, the bending being analogous to that in a mirage; if this were the cause of the deflexion, γ -rays of the same frequency as the electronic waves would also be deflected by the electric force. If, however, the deflexion of the electron were due to the action of the electric field on the negative charge on the nucleus, and not to the effect on the sphere surrounding it, the γ -rays would not be deflected by the electric field. The experiments are in favour of this view rather than the former.

THE discovery by G. P. Thomson and Davisson & Germer of electronic waves implies that the electron must be something much more complex than the point charge of negative electricity which had previously been regarded as its adequate representation. In 'Beyond the Electron' and in a paper (Phil. Mag. xxxiii. p. 191) I have suggested a constitution for the electron which would cause a moving electron to be accompanied by a train of waves. I propose in this paper to develop the consequences of this hypothesis, and to describe some experiments I have made in connexion with it.

On this view the electron consists

(I.) of a nucleus which, like the old conception of the electron, is a charge e of negative electricity concentrated in

a small sphere. If a is the radius of this sphere, the energy due to the nucleus alone would be equal to qe^2/a , where q is a numerical constant if e is measured in electrostatic units. Its value will depend upon the way the electric charge is distributed throughout the region occupied by the sphere whose radius is a . It would, for example, be least if all the charge were on the surface of the sphere, it would be greater if the charge were uniformly distributed through the sphere, and greater still if the density increased towards the centre. This nucleus will have definite periods of vibration, for when it is in equilibrium the lines of force starting from it will be symmetrically distributed around it; if this symmetry is disturbed, the new arrangement will not be in equilibrium, but will oscillate about the old one. The time of the vibration will be proportional to the time light takes to travel round the nucleus, *i.e.* to $2\pi a/c$, where c is the velocity of light. Let the time of vibration be $k2\pi a/c$, where k is a numerical constant; the frequency ν is therefore $c/2\pi ak$, and since E the energy is equal to qe^2/a , we have the relation

$$E = 2\pi qke^2 \frac{\nu}{c}.$$

This is a relation of the form $E = h\nu$; $2\pi qke^2/c$ corresponding to Planck's constant h .

(II.) The nucleus does not constitute the whole of the electron; surrounding it there is a structure of much larger dimensions which we shall call the sphere of the electron, made up of parts which under electric forces of very high frequency are set in motion and produce effects of the same type as are produced by convective currents of electricity. We shall suppose that these parts can be represented by a number of negative charges each with a mass μ and an electric charge $-\epsilon$, and an equal number of positive charges each with a mass μ' and a charge $+\epsilon$.

Field Equations for a Stationary Electron.

Let (X, Y, Z) (α, β, γ) be respectively the components of electric and magnetic forces, N the number of either positive or negative charges per unit volume, and x_r, y_r, z_r coordinates fixing the position of one of the charges. Then by Maxwell's equations we have

$$\frac{1}{c^2} \frac{dX}{dt} + 4\pi \sum \epsilon \frac{dx_r}{dt} = \frac{d\gamma}{dy} - \frac{d\beta}{dz}, \quad \dots \quad (1)$$

with similar equations for Y and Z .

Again

$$\frac{dX}{dy} - \frac{dY}{dx} = \frac{d\gamma}{dt} \dots \dots \dots (2)$$

When the frequency of the vibrations is large compared with that of the individual system formed by a doublet of $+\epsilon$ and $-\epsilon$,

$$\mu \frac{d^2x}{dt^2} = X\epsilon \dots \dots \dots (3)$$

From (1), (2), and (3) we get three equations of the type

$$\begin{aligned} \frac{d^2X}{dt^2} + p_0^2 X \\ = c^2 \left\{ \frac{d^2X}{dx^2} + \frac{d^2X}{dy^2} + \frac{d^2X}{dz^2} - \frac{d}{dx} \left(\frac{dX}{dx} + \frac{dY}{dy} + \frac{dZ}{dz} \right) \right\}, \end{aligned} \dots \dots (4)$$

$$\text{where } p_0^2 = 4\pi c^2 \left(\frac{N\epsilon^2}{\mu} + \frac{N\epsilon_1^2}{\mu'} \right), \dots \dots \dots (5)$$

and three of the type

$$\frac{d^2\alpha}{dt^2} + p_0^2 \alpha = c^2 \left(\frac{d^2\alpha}{dx^2} + \frac{d^2\alpha}{dy^2} + \frac{d^2\alpha}{dz^2} \right) \dots \dots \dots (6)$$

From equations (4) we get

$$\frac{d^2}{dt^2} \left(\frac{dX}{dx} + \frac{dY}{dy} + \frac{dZ}{dz} \right) + p_0^2 \left(\frac{dX}{dx} + \frac{dY}{dy} + \frac{dZ}{dz} \right) = 0. \quad (7)$$

This equation is of the type

$$\frac{d^2\psi}{dt^2} + p_0^2 \psi = 0,$$

and represents a vibration whose frequency is p_0 . Thus the region round the nucleus of the electron—"the sphere"—has a natural frequency p_0 .

Vibrations of Ionized Gas.

The fact that a mixture of positive and negative charges vibrates with a definite frequency has applications to many problems besides the one under discussion. An ionized gas which contains free electrons and positive ions is a system quite analogous to the one we are considering. When an electric current passes through a discharge-tube containing gas at a low pressure, the negative glow, the positive column, the striations, etc. are all places where there are free

electrons and positive ions, and which therefore have definite times of vibration. For the ionized gas $\epsilon = e$ the charge on the electron and μ is equal to its mass; in this case the mass of the positive charge is so great compared with the electron that we may neglect the term in μ in equation (5), and substituting the numerical values of e and m in that equation, we find that the number of vibrations per second in the ionized gas is $2.8\sqrt{N \times 10^7}$; if f is the fraction of the molecules ionized, p the pressure in millimetres of mercury,

$$N = f \cdot \frac{p}{760} \times 2.75 \times 10^{19},$$

so that the number of vibrations per second is

$$1.6 \times 10^{12} \sqrt{pf}.$$

When the system vibrates with the frequency p_0 it is easy to show that

$$\frac{1}{c} \frac{dX}{dt} + 4\pi \Sigma N \epsilon \cdot \frac{dx}{dt} = 0,$$

thus the convection currents balance the displacement ones so that there is no effective current. There are no currents to produce magnetic force so that the magnetic force will vanish, and with it the Poynting vector. Thus there is no transference of energy, and therefore no radiation. We have here the very interesting case of electrical vibrations without radiation. The oscillations in the ionized gas in the discharge-tube would be accompanied by oscillating electrical forces of the same period. These would not be detected by the ordinary methods of measuring the distribution of electric force along the tube. Thus, for example, such measurements show that the steady electric force in the negative glow is exceedingly small. It is possible, however, that owing to these electrical oscillations there may be forces of considerable magnitude but high frequency acting throughout the negative glow, and that these may have some influence in producing its luminosity. We can produce by the aid of hot-wire valves electrical forces of very high frequency. If these were applied to any ionized gas, pronounced effects might be expected when the frequency of the forces coincided with that of the free vibrations of the gas.

We have seen that when a system of the type we have assumed for the sphere of the electron is vibrating in its natural period the magnetic forces vanish, and hence the

electric forces must be derivable from a potential, so that we may write

$$X = \frac{d\phi}{dx}, \quad Y = \frac{d\phi}{dy}, \quad Z = \frac{d\phi}{dz}.$$

*Velocity of Phase Propagation and Group Velocity
in the Super-dispersive Medium.*

If a plane wave whose frequency is p is travelling through the medium parallel to the axis of z , we may put

$$X = \cos p \left(t - \frac{z}{V} \right), \quad Y = 0, \quad Z = 0,$$

where V is the phase velocity. Substituting these values in equation (4), we find

$$V^2 = c^2 \cdot \frac{p^2}{p^2 - p_0^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

or in terms of the wave-length $\lambda = 2\pi \cdot V/p$,

$$V^2 = c^2 + \frac{p_0^2 \lambda^2}{4\pi^2} \cdot \cdot \cdot \cdot \cdot \cdot (9)$$

If μ is the refractive index c/V , then from (8)

$$\mu^2 = 1 - \frac{p_0^2}{p^2} \cdot \cdot \cdot \cdot \cdot \cdot (10)$$

We see from (8) that waves whose frequency is less than p_0 cannot be propagated through the "sphere" of the electron. This need not apply if p is very much smaller than p_0 , for equation (3) is only true where the frequency of the vibrations is large compared with that of the free vibrations of the units forming the sphere of the electron. When this is not the case the field equations reduce to the ordinary equations of wave-motion.

The group velocity, which is also the velocity with which energy travels along the wave, is equal to

$$1/\frac{d}{dp} (p/V) = c \frac{\sqrt{p^2 - p_0^2}}{p} = c^2/V. \quad \cdot \quad (11)$$

*Distribution of Energy when the "Sphere" is vibrating
in its Free Period.*

Let the components of the electric force be represented by

$$X = A \cos p_c t, \quad Y = B \cos p_0 t, \quad Y = C \cos p_0 t,$$

where A, B, C may vary from place to place. The energy per unit volume due to the electric force is

$$(X^2 + Y^2 + Z^2) / 8\pi c^2,$$

and is thus equal to

$$\frac{1}{8\pi c^2} (A^2 + B^2 + C^2) \cos^2 p_0 t.$$

The kinetic energy per unit volume of the moving electrified parts is

$$\begin{aligned} \frac{1}{2} N \mu \left(\left(\frac{dx_r}{dt} \right)^2 + \left(\frac{dy_r}{dt} \right)^2 + \left(\frac{dz_r}{dt} \right)^2 \right) \\ + \mu' \left(\left(\frac{dx_r'}{dt} \right)^2 + \left(\frac{dy_r'}{dt} \right)^2 + \left(\frac{dz_r'}{dt} \right)^2 \right). \end{aligned}$$

From the equations

$$\mu \frac{d^2 x_r}{dt^2} = X\epsilon,$$

$$\mu' \frac{d^2 x_r'}{dt^2} = X\epsilon,$$

we find that the kinetic energy is equal to

$$\frac{1}{2} \cdot \frac{\left(\frac{N\epsilon^2}{\mu} + \frac{N\epsilon^2}{\mu'} \right)}{p_0^2} (A^2 + B^2 + C^2) \sin^2 p_0 t.$$

But by equation (5) this equals

$$\frac{1}{8\pi c^2} (A^2 + B^2 + C^2) \sin^2 p_0 t.$$

Thus the sum of the energy of the electric field and the kinetic energy of the moving parts is, per unit volume,

$$\frac{1}{8\pi c^2} (A^2 + B^2 + C^2), \quad . \quad . \quad . \quad . \quad (12)$$

and thus does not alter with the time, so that the energy in the "sphere" of the electron will be constant.

If the oscillations have the frequency p instead of p_0 , the kinetic energy per unit volume of the moving electrified parts is equal to

$$\frac{1}{8\pi c^2} \cdot \frac{p_0^2}{p^2} (A^2 + B^2 + C^2) \sin^2 pt. \quad . \quad . \quad . \quad (13)$$

As p is always greater than p_0 , the average kinetic energy

is less than the average energy due to the electrostatic field. The nucleus and the sphere of the electron form a connected system, and energy can flow from the one into the other; when a steady distribution of energy is reached the nucleus of the electron will be in resonance with the sphere. The frequency of vibrations of the sphere, p_0 , depends upon the *density* of the electrified units of which it is composed, and not upon the total number in the sphere; thus by expansion or contraction it may adjust its period so as to be in resonance with the nucleus. On this view p_0 will have a definite value, which will be the same whether the electron is free or whether it forms a part of an atom or molecule containing many other electrons. There is evidence, as we shall see, that the sphere of the electron is, on a low estimate, comparable in size with the dimension of an atom or molecule; so that in a molecule containing many electrons their spheres would overlap and form practically a continuous medium in which p_0 would be constant and equal to the frequency of the vibrations of the nucleus of the electron. When such molecules unite to form a solid, the whole solid, from the point of view of the transmission of waves of very high frequency, may be regarded as an enormously large electronic sphere. We shall return to this point later.

The Electron in Motion.

Let us now consider what will happen to an electron of this type if it is in motion instead of at rest; we shall suppose that it is moving uniformly parallel to the axis of x with the velocity u . The motion of the lines of electric forces will produce magnetic forces whose direction at any point is at right angles to the lines of electric force at that point and to the direction of their motion; the magnetic forces will thus be at right angles to the axis of x . These magnetic forces, like the electric forces whose motion produces them, are alternating with great rapidity, and, as an alternating magnetic force produces electric forces which cannot be derived from a potential, the electric forces will not be given by the same expressions as for the electron at rest, but will be modified in a way we proceed to determine.

The displacement current parallel to z in the moving electron will not be dZ/dt if d/dt denotes a partial differential coefficient, but $\left(\frac{d}{dt} - u \frac{d}{dx}\right)Z$. Similarly, the rate of increase

of the magnetic force will not be $d\beta/dt$, but $\left(\frac{d}{dt} - u \frac{d}{dx}\right)\beta$.

Again, as the electric charges in the sphere of the electron are moving, the form parallel to z on one of these units is not $Z\epsilon$ but $(Z-u\beta)\epsilon$.

Hence the equations of the field become

$$\frac{1}{c^2} \left(\frac{dZ}{dt} - u \frac{dZ}{dx} \right) + 4\pi \Sigma \epsilon \frac{dz}{dt} = \frac{d\beta}{dx} - \frac{d\alpha}{dy},$$

$$\frac{1}{c^2} \left(\frac{dY}{dt} - u \frac{dY}{dx} \right) + 4\pi \Sigma e \frac{dy}{dt} = \frac{d\alpha}{dz} - \frac{d\gamma}{dx},$$

$$\frac{d\gamma}{dt} - u \frac{d\gamma}{dx} = \frac{dX}{dy} - \frac{dY}{dx},$$

$$\frac{d\beta}{dt} - u \frac{d\beta}{dx} = \frac{dZ}{dx} - \frac{dX}{dz},$$

$$\mu \frac{d^2 z}{dt^2} = -\epsilon(Z-u\beta).$$

We can find by inspection a solution when u/c is exceedingly small; it is evidently

$$\alpha = 0, \quad \beta = -\frac{u}{c^2} Z, \quad \gamma = \frac{u}{c^2} Y,$$

$$\frac{u}{c^2} \frac{dY}{dt} = -\frac{dY}{dx},$$

$$\frac{u}{c^2} \frac{dZ}{dt} = -\frac{dZ}{dx}.$$

Hence, if

$$Y = \cos p_0 t \cdot \frac{d}{dy} f(x, y, z); \quad Z = \cos p_0 t \cdot \frac{d}{dz} f(x, y, z)$$

is the solution when the electron is at rest, then, retaining only the lowest powers of u/c , the solution for the moving electron is

$$Y = \cos p_0 \left(t - \frac{ux}{c^2} \right) \frac{d}{dy} \cdot f((x-ut), y, z),$$

$$Z = \cos p_0 \left(t - \frac{ux}{c^2} \right) \frac{d}{dz} f((x-ut), y, z),$$

$$\alpha = 0, \quad \beta = -\frac{u}{c^2} \cos p_0 \left(t - \frac{ux}{c^2} \right) \frac{d}{dz} (f((x-ut), y, z)),$$

$$\gamma = \frac{u}{c^2} \cos p_0 \left(t - \frac{ux}{c^2} \right) \frac{d}{dy} f((x-ut), y, z).$$

By using the Lorentzian transformation we can find a solution which is not limited to the case when u/c is exceedingly small; it is

$$\left. \begin{aligned} Y &= k \cos p \left(t - \frac{ux}{c^2} \right) \frac{d}{dy} f(k(x-ut), y, z), \\ Z &= k \cos p \left(t - \frac{ux}{c^2} \right) \frac{d}{dz} f(k(x-ut), y, z), \\ \alpha &= 0, \quad \beta = -\frac{u}{c^2} Z, \quad \gamma = \frac{u}{c^2} Y, \end{aligned} \right\} \quad (14)$$

where

$$k = \frac{1}{\sqrt{1 - \frac{u^2}{c^2}}} \quad \text{and} \quad p = p_0 k.$$

Thus the frequency of the moving electron is greater than that of the stationary. We see that the expressions for the electric and magnetic force round the moving electron contain the factor $\cos p \left(t - \frac{ux}{c^2} \right)$; this factor represents plane waves travelling in the direction of motion of the electron. The phase velocity is equal to c^2/u , and thus depends only on the velocity of the electron, and not upon the density of the electric charges in its sphere. The wave-length λ of the waves is given by the equation

$$\lambda = \frac{2\pi c^2}{pu}, \quad \text{or} \quad \lambda u = \frac{2\pi c^2}{p_0} \sqrt{\frac{1-u^2}{c^2}}.$$

This is exactly the relation established by G. P. Thomson's experiments on the diffraction of electrons. We saw, equation (11), that if V is the phase velocity and U the velocity with which the energy travels through the medium,

$$U = \frac{c^2}{V}.$$

We have just seen that $V = c^2/u$; hence $U = u$, so that the energy travels along with the electron. This investigation shows that if the electron is of the type we are considering, then it follows from the laws of classical electrodynamics that when it is in motion it will be accompanied by a train of waves, and that the relation between the wave-length and the velocity is exactly that indicated by G. P. Thomson's experiments. The electronic waves on this view are waves

of electric and magnetic forces; they differ from electric waves through the normal ether, not only in the phase velocity, but also in that in the electronic waves the magnetic force is smaller relatively to the electric than in normal electric waves.

We proceed to illustrate these principles by considering the waves that would accompany electrons of special types.

Take first the case when in the stationary electron the alternating electric force is parallel to the axis of z , so that the electron is polarized. The equations for the stationary electron are

$$Z = A \cos p_0 t, \quad Y = 0, \quad X = 0, \\ \alpha = \beta = \gamma = 0.$$

The energy per unit volume: the sum of the energy due to the electrostatic field and the kinetic energy of the moving charges is, by equation (12), equal per unit volume to $A^2/8\pi$. If the nucleus moves with uniform velocity u parallel to the axis of x , the electric and magnetic forces are by (14) given by

$$Z = Ak \cos p \left(t - \frac{ux}{c^2} \right), \quad Y = 0, \quad X = 0; \\ \beta = -\frac{uk}{c^2} A \cos p \left(t - \frac{ux}{c^2} \right), \quad \alpha = 0, \quad \gamma = 0,$$

where

$$k = 1 / \sqrt{1 - \frac{u^2}{c^2}}, \quad p = kp_0.$$

Thus the electric and magnetic forces are represented by trains of waves of constant amplitude. As in electric waves through the normal ether, the magnetic force is at right angles to the electric and proportional to it; but in the electronic waves the ratio of the magnetic to the electric force is only u/c of the same ratio for normal electrical waves.

The energy per unit volume due to the electrostatic field is

$$\frac{1}{8\pi} A^2 k^2 \cos^2 p \left(t - \frac{ux}{c^2} \right).$$

From equation (13) the energy due to the moving electrified systems is

$$\frac{1}{8\pi} \frac{p_0^2}{p^2} A^2 k^2 \sin^2 p \left(t - \frac{ux}{c^2} \right).$$

The energy due to the magnetic field is

$$\frac{1}{8\pi} \frac{u^2}{c^2} k^2 \cos^2 p \left(t - \frac{ux}{c^2} \right).$$

Since $p_0^2/p^2 = 1 - \frac{u^2}{c^2}$, we see that the mean energy due to the electrostatic field is equal to the mean of the sums of the kinetic and magnetic energies.

Symmetrical Electron.

Another very interesting case is when the field round the stationary electron is defined by the equations

$$X = A \cos p_0 t \cdot \frac{d}{dx} \frac{1}{r}, \quad Y = A \cos p_0 t \cdot \frac{d}{dy} \frac{1}{r}, \quad Z = A \cos p_0 t \cdot \frac{d}{dz} \frac{1}{r},$$

. . . (15)

and consequently

$$\alpha = \beta = \gamma = 0.$$

Here r is the distance from the centre of the nucleus. These equations represent an electric field where the distribution of the alternating electric force is the same as that of the steady electric field due to the charge on the nucleus. Thus on this view there is in the electron a steady radial electric force equal to e^2/r^2 , and superposed on this an alternating electric force also radial and also proportional to $1/r^2$.

The sum of the energy per unit volume due to the electric field and to the kinetic energy of the electric charges in the sphere is, by equation (12), equal to

$$\frac{1}{8\pi} A^2 \left\{ \left(\frac{d}{dx} \frac{1}{r} \right)^2 + \left(\frac{d}{dy} \frac{1}{r} \right)^2 + \left(\frac{d}{dz} \frac{1}{r} \right)^2 \right\}$$

$$= \frac{A^2}{8\pi} \frac{1}{r^4}.$$

The energy per unit volume due to the charge on the nucleus is equal to $e^2/8\pi r^4$.

Thus the energy due to the charge on the nucleus and that due to the alternating field have a constant ratio to each other, and the total energy of the electron is

$$\frac{1}{2} \frac{e^2}{a} + \frac{1}{2} \frac{A^2}{a},$$

where a is the radius of the nucleus.

The energy outside a sphere whose centre is at the nucleus and radius b is $(e^2 + A^2)/2b$.

The Size of the Nucleus of the Electron.

The usual way of calculating the size of the electron is from the equation

$$\text{Energy of the electron} = mc^2,$$

where m is the mass of the electron. If a is the radius of the nucleus, the energy of the electric field due to it is $e^2/2a$, so that if the electron consisted of nothing but the nucleus, we should have

$$\frac{e^2}{2a} = m_0 c^2 \quad \text{or} \quad 2a = e^2/m_0 c^2,$$

where m_0 is the mass of a stationary electron ; this equation leads to the value 1.4×10^{-13} cm. for a .

When, as in the type of electron we are considering, the nucleus is surrounded by a sphere, the energy is not $e^2/2a$ but $(e^2 + A^2)/2a$, so that $2a = (e^2 + A^2)/m_0 c^2$. Thus for an electron of this kind the radius of the nucleus is greater than the conventional value, and if A is large compared with e it may be very much greater.

Planck's Constant.

The energy of the electron is $(e^2 + A^2)/2a$ and the time of vibration that of the nucleus ; this will be proportional to the time light takes to travel round $2\pi a$, the circumference of the nucleus. Let it equal $2\pi qa/c$, where q is a constant. Thus the frequency $p_0 = c/2\pi qa$, while E the energy is equal to $(e^2 + A^2)/2a$; hence

$$E = \frac{p_0}{c} \cdot \pi q (e^2 + A^2),$$

so that Planck's constant is $(e^2 + A^2)\pi q/c$. This expression leads to the conclusion that A must be large compared with e , *i. e.* that the greater part of the energy must be in the sphere. For if A were zero the value of Planck's constant would be $\pi q e^2/c$, *i. e.* $2.4q \times 10^{-29}$; the actual value is 6.65×10^{-27} . Hence we conclude that A is probably at least 100 times e^2 , or that only some 1 per cent. of the energy is due to the electric field of the nucleus.

We arrive at the same conclusion from the fact that p_0 , the frequency of vibration of the nucleus, is from G. P. Thomson's experiments 1.1×10^{20} ; so that in the time of one

vibration light will travel over 3×10^{-10} cm. This distance will be comparable with the circumference of the nucleus ; so that a can hardly be less than 10^{-11} , which is about one hundred times the radius calculated on the assumption that all the energy is in the nucleus. The "sphere" of the electron is a system with a much larger number of degrees of freedom than the nucleus ; so that if there is anything corresponding to equi-partition of energy, we should expect the sphere to contain the bulk of the energy.

Planck's Constant for Light.

It follows as a result of G. P. Thomson's experiments that p_0 , the frequency of vibration of the electron, bears to the energy of the electron the same, or nearly the same, ratio as the frequency of a quantum of light bears to the energy in the quantum. With an electron of the type we are considering we can see some reason why this should be the case. For suppose that the energy E' required for a quantum of light is abstracted by some process from an electron. It seems not unreasonable to suppose that when the electron loses energy the loss begins at the outside and goes on until enough has been obtained in this way to supply the energy E' required for the quantum. We may thus imagine that the energy comes from an outer sheath of the electron and absorbs all the energy in the sheath. Let b be the internal radius of the sheaths ; the energy in the quantum will be that in the electron between the region $r=b$ and $r=\infty$, *i. e.* $(e^2 + A^2)/2b$. The sheath when detached will have a hole inside it whose radius is b , and the time of its vibration will be proportional to the time light takes to branch over the circumference of this cavity ; thus p the frequency will be given by the equation $p = c/2\pi bq_1$. Hence

$$E' = p(e^2 + A^2)q\pi/c.$$

Thus, on this view, the relation between the energy in the quantum and its frequency will be the same as for the electron. Though the energy in the quantum is the same as that in the sheath of the electron from which it is derived, the disposition of the lines of electric force in the quantum when it has settled down into a steady state will be very different, the lines of electric force will no longer be radial, but will form closed curves, the frequency of the vibrations will be too small for the medium to show its super-dispersive properties, and the energy which was previously in the sheath in the form of the kinetic energy of the moving

particles will become the energy due to the magnetic forces in the light-quantum.

The Moving Electron.

If an electron where the electric and magnetic forces when it is stationary are represented by the equations (15) is moving uniformly parallel to the axis with the velocity u , the periodic electric and magnetic forces will, by equations (14), p. 1267, be given by the equations

$$Y = kA \cos p \left(t - \frac{ux}{c^2} \right) \frac{y}{R^3},$$

$$Z = kA \cos p \left(t - \frac{ux}{c^2} \right) \frac{z}{R^3},$$

$$\alpha = 0, \quad \beta = -\frac{u}{c^2} Z, \quad \gamma = \frac{\mu}{c^2} Y,$$

where
$$k = 1 / \sqrt{1 - \frac{u^2}{c^2}}, \quad p = kp_0,$$

and
$$R^2 = k^2(x - ut)^2 + y^2 + z^2.$$

Thus again we have a plane wave travelling in the direction of x , with the same relation between the wave-length and velocity as before; the amplitude of the waves diminishes as the distance from the nucleus increases.

The non-periodic forces in the electron due to the charge on the nucleus are given by

$$X = ke \frac{(x - ut)}{R^3}, \quad Y = ke \frac{y}{R^3}, \quad Z = ke \frac{z}{R^3},$$

$$\alpha = 0, \quad \beta = -\frac{u}{c^2} Z, \quad \gamma = \frac{u}{c^2} Y.$$

Size of the Sphere of the Electron.

If when the electron is passing through a thin film as in the experiment on the diffraction of electrons, the film behaves like a non-dispersive ether, then the consideration of the separation of spectra of different orders in the diffraction pattern will lead to an inferior limit to the size of the sphere of the electron. To separate these spectra will require a train of waves containing not less than a certain number of wave-lengths. G. P. Thomson calculates from the separation he obtained in his experiments that the train of waves must have extended over at least 5×10^{-8} cm.

If the medium in the film through which the electron is passing is the normal ether, then this train of waves must be in the sphere of the electron, as this is the only super-dispersive medium. Thus the diameter of the sphere of the electron must be at least 5×10^{-8} cm., and thus large compared with the diameter of a molecule. But if this is so, the assumption that the ether in the film is not dispersive, is not tenable. The molecules in the film contain many electrons, and if the spheres of these were large compared with the dimensions of a molecule, they would overlap; thus the film would be filled not with the normal ether, but with the super-dispersive medium of electronic spheres. When the moving electron enters this medium it will excite waves in it of frequency p , where $p = kp_0$ is the frequency of the moving electron. The field equation in the whole of the film is of the form

$$\frac{d^2\phi}{dt^2} + p_0^2\phi = c^2\nabla^2\phi,$$

and we see that a vibration of frequency p will excite in this medium waves whose length λ is given by

$$\lambda = \frac{2\pi c}{\sqrt{p^2 - p_0^2}} = \frac{2\pi c^2}{u p_0 k},$$

which is the same as the wave-length of the waves accompanying the moving electron. Since the whole of the metallic film is filled with the super-dispersive medium, there is room for a train of waves equal in length to the thickness of the film; the length of the train is no longer determined by the size of the sphere round a single electron.

It must be remembered, too, that the problem of determining the length of the train of waves necessary to separate two diffraction rings produced by light is not, on the Classical Theory of Light, identical with that required to produce the separation for electronic waves. The rings observed with electronic waves mark the paths of the nuclei of the electrons: an electron has to remain intact, and a single electron cannot spread out over the whole of the region where diffraction theory indicates the presence of waves. If the chance of an electron going in any direction were directly proportional to the intensity of the waves travelling in that direction, then the conditions for separation would be the same for electronic as for light-waves. But it may be, since the two parts of the electron, the nucleus and the sphere through which the waves travel, have to remain

together, that the electron will have a special tendency to move in a direction in which the intensity of the waves is symmetrical on either side of the direction in which the electron is moving; this direction is one along which the intensity of the waves is a maximum; this would make the intensity of a ring change more rapidly in the neighbourhood of the maximum than for the corresponding light-waves, and would increase the resolution. It would follow from this that the size of the sphere need not be quite so large as would be indicated by purely optical considerations; it must, however, I think, from the result of experiments, be at least comparable with atomic dimensions. If this is so, then the ether inside an atom must be in the super-dispersive state; and when as in a solid we have a closely-packed aggregation of molecules, the ether throughout the solid will also be in this state for vibrations of frequency comparable with p_0 . The field equations for the electric and magnetic force will be of the type

$$\frac{d^2\phi}{dt^2} + p_0^2\phi = c^2\nabla^2\phi,$$

and determine the propagation of all such vibrations through the medium.

The form of the field equations, when there is an external electric field, depends upon whether the force exerted on an electron by an electric field is due to the direct action of the force on the negative charge of the nucleus, or whether it is due to the bending of the electronic waves by refraction, owing to the gradient in the refractive index produced by the electric field.

On the first view the super-dispersive properties of the medium are not affected by the presence of an electric field. So that the field equations are of the form

$$c^2\left(\frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} + \frac{d^2\phi}{dz^2}\right) = \frac{d^2\phi}{dt^2} + p_0^2\phi.$$

Thus, to take a special case, that of an electron moving under the attraction of a proton, when the velocity of the electron is u , the frequency of the vibrations it emits is

$$p_0 \sqrt{1 - \frac{u^2}{c^2}};$$

hence

$$\frac{d^2\phi}{dt^2} = - \frac{p_0^2}{1 - \frac{u^2}{c^2}},$$

and the equation becomes

$$c^2 \nabla^2 \phi + \frac{p_0^2 \frac{u^2}{c^2}}{\left(1 - \frac{u^2}{c^2}\right)} \phi = 0.$$

If m is the mass of the electron, R its distance from the proton, E_0 a constant,

$$\frac{1}{2} m u^2 = E_0 + \frac{e^2}{R},$$

so that the field equation becomes

$$c^2 \nabla^2 \phi + \frac{\frac{2p_0^2}{mc^2} \left(E_0 + \frac{e^2}{R}\right)}{1 - \frac{2\left(E_0 + \frac{e^2}{R}\right)}{mc^2}} \phi = 0,$$

or approximately

$$c^2 \nabla^2 \phi + \frac{2p_0^2}{mc^2} \left(E_0 + \frac{e^2}{R}\right) \phi = 0.$$

When the deflexion of the electron is due to the refraction of the wave μ , the refractive index of the dispersive medium at the point x, y, z is given by the equation

$$\mu^2 = \mu_0^2 + 2V/mc^2,$$

where

$$\frac{dV}{dx}, \quad \frac{dV}{dy}, \quad \frac{dV}{dz}$$

are the components of the force which would act on an electron if it were at the point x, y, z .

The field equations when the frequency is p can be written in the form

$$c^2 \nabla^2 \phi + 4\pi^2 \mu^2 p^2 \phi = 0,$$

or, substituting the value of μ^2 ,

$$c^2 \Delta^2 \phi + 4\pi^2 p^2 (\mu_0^2 + 2V/mc^2) \phi = 0.$$

When the electric field is that due to a proton, $V = -e^2/r$, where $r^2 = x^2 + y^2 + z^2$, and the equation becomes

$$c^2 \nabla^2 \phi + 4\pi^2 p^2 \left(\mu_0^2 + \frac{2e^2}{r} / mc^2 \right) \phi = 0.$$

The frequency p_0 is equal to 1.1×10^{23} , the quantum of light for this frequency is about 500,000 volts; hence light

whose quantum is greater than this would, when it passed through a solid, behave as if it were travelling through a super-dispersive medium, *i.e.* its phase velocity would be greater than that of light; on the other hand, light whose quantum is considerably less than this would behave as if it were travelling through the normal ether. Now, among the γ -rays given out by radium C there are some whose quantum is less than the critical value, others whose quantum is greater. We should expect these two types to behave differently when passing through a solid, *e.g.* that the scattering of the harder rays would not follow the same laws as that of the softer, a point which could be settled if we could measure the scattering of rays of different types. It is, however, difficult to get anything like a monochromatic spectrum of γ -rays, so that tests of this kind would involve very difficult experiments. There is, however, another test which can be applied much more easily; the interpretation of the results of this test is, however, more ambiguous than that for the scattering test; the test we refer to is the effect of electric force on the γ -rays. We know that when an electric force acts upon an electron the electron is deflected. Is this deflexion due primarily to the deflexion of the electronic waves, or is it, as on the usual theory, due to the action of the electric force on the negative charge on the nucleus? The electronic waves must always travel in the direction in which the nucleus is moving, so that if the path of the waves is altered, as in the experiments on diffraction, the path of the nucleus will be altered too, so that anything which deflected the waves would deflect the path of the nucleus and produce effects of the same type as would be produced by forces acting directly on the nucleus. The direction of the waves could be altered by refraction as well as by diffraction, and if the electric force produced a gradient in the refractive index of the medium, the path of the electronic waves would be curved like the rays in a mirage. If the application of an electric force X made the refractive index, μ , of the medium through which the electron is moving vary according to the law,

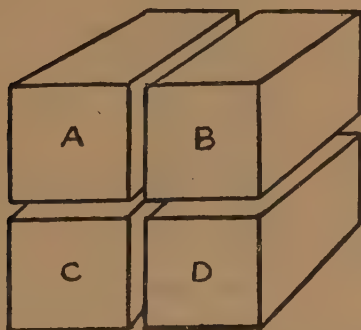
$$\mu \frac{d\mu}{dx} = \frac{Xe}{mc^2},$$

then the path of the electron would, in consequence of the refraction of the waves, be the same as if the electron were acted on by an electric force equal to X .

On this view the electric force deflects the electron by producing a gradient in the refractive index of the

super-dispersive medium which surrounds it ; this bends the electronic waves, and they carry the nucleus along with them. If this view is true, the gradient in the refractive index would bend to the same extent as it does the electron any waves of the same period as the electronic waves, whether they were accompanied by an electron or not. The alternative view is that, as in ordinary electrostatic theory, the electric force acts on the negative charge on the nucleus and the nucleus drags the waves along with it, since the two must travel in the same direction. On this view, the charge on the electron is essential for the deflexion, so that waves of the same period as the electronic waves, but not accompanied by an electron, would not be deflected by an electric field. Thus, on the first view, γ -rays of the same period as

Fig. 1.

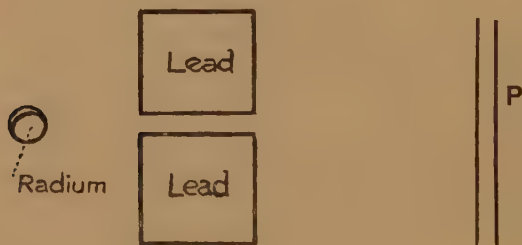


electronic waves would be deflected by an electric force ; on the second they would not. Now, among the γ -rays from radium C there are some which, since their quantum of energy is greater than 500,000 volts, have the same frequency as the electronic waves which accompany an electron moving at a suitable speed. It is thus interesting to determine whether such γ -rays would, like the electron with its waves, be deflected by electric force. We may hope to detect such a deflexion if it exists among some of the constituents of a mixed group of γ -rays, even though we are not able to isolate the various types of rays. The γ -rays with quanta less than 500,000 volts would not be deflected on either view. I have made some experiments to test the effect of electric force on the path of γ -rays, using the following arrangement :—

A, B, C, D (fig. 1), are four lead rectangular parallelepipeds 4 cm. by 2 cm. by 2 cm. The surfaces of the parallelepipeds

which face each other were carefully worked so as to be smooth planes; the inside faces of A and C were in the same vertical plane, as were also those of B and D. A was carefully insulated from B, C, D, and B from A, C, D; C and D were connected with the earth so as to be at the same potential; A and C were connected with the terminals of a dynamo giving constant potential differences up to 5500 volts; the interval between the blocks AC and BD was filled by thin flat plates of a dielectric; mica, sulphur, paraffin, glass, and quartz were tried; the faces of the lead blocks were pressed against the plate of dielectric. As some of the mica plates were only .3 mm. thick, electric forces up to 183,000 volts per centimetre could be obtained. The narrow space between the faces of AC and BD formed a slit through which could pass the γ -rays from radium emanation contained in a small glass vessel whose centre was on the

Fig. 2.



line of intersection of the planes of the horizontal slit between the blocks AB and CD and of the vertical slit between AC and BD. The rays after passing through the slit fell on a photographic plate, at some distance from the lead blocks and set so as to be at right angles to both the vertical and horizontal slits between the blocks. A plate of lead 1.5 mm. thick was placed parallel to the photographic plate P (fig. 2), and about a centimetre away from it, to prevent β -rays reaching the plate. The rays passing through the upper part of the slit between the blocks A and B (fig. 1) are subject to a very intense electric force from which those passing through the lower half are free. If the harder γ -rays are deflected by electric force, we might expect that there would be a difference between the upper and lower halves of the image of the slit formed on the photographic plate by the γ -rays. If there were some bending, but not enough to drive the rays against the sides of the slit, we should expect to find

on the upper part of the plate, but not on the lower, lines parallel to the image of the slit, formed by rays which had been deflected by the electric force, as in fig. 3, while if the deflexion were great enough to drive the rays against the side of the slit, the upper half of the image of the slit would be fainter than the lower.

If the bending of the path of the electron by electric force is due to the bending of the electronic waves, owing to the refractive index of the medium varying from point to point in an electric field, the connexion between the

Fig. 3.



refractive index μ and the applied electric force X is (see 'Beyond the Electron') given by the equation

$$\frac{d\mu^2}{dx} = \frac{Xe}{mc^2/2} \quad \dots \quad (16)$$

The radius of curvature ρ of a ray travelling through such a medium at right angles to the direction of x is given by

$$\frac{1}{\rho} = \frac{1}{\mu} \frac{d\mu}{dx}$$

or

$$\frac{1}{\rho} = \frac{Xe}{\mu^2 mc^2}.$$

If p is the frequency of the waves and h Planck's constant,

$$hp = mc^2, \quad \mu^2 = 1 - \frac{p_0^2}{p^2},$$

where p_0 is the critical frequency ; hence, when $p > p_0$,

$$\frac{1}{\rho} = \frac{Xe}{hp \left(1 - \frac{p_0^2}{p^2}\right)}.$$

If the energy of the quantum of the γ -ray is represented by V volts, $hp = Ve$, so that

$$X\rho = V \left(1 - \frac{p_0^2}{p^2}\right). \quad . \quad . \quad . \quad . \quad (17)$$

The value of V for the critical frequency p_0 is about 500,000 volts. The value of ρ given by (17) is the curvature of the γ -ray in the super-dispersive medium. If the dielectric through which the ray is passing is not super-dispersive through the whole of the region, but only so in patches, the average value of ρ would be greater than this by an amount depending on the fraction of the volume occupied by the super-dispersive portion.

In some of the experiments the thickness of mica between the blocks was .3 mm. and the potential difference between the blocks A and B 5500 volts ; thus X would be 183,000 volts per cm. ; for the strong γ -ray for which $V = 610,000$ ρ would be 1 cm., and with this curvature a ray would be bent through .3 mm. and thus driven against the plate after passing through about 2.4 mm. As the length of the path in the dielectric was 40 mm., these γ -rays would be unable to pass through the upper part of the slit if even a small fraction of the dielectric were super-dispersive.

The first experiment I tried was one where the γ -rays passed through a plate of mica 1 mm. thick exposed to a potential difference of 5500 volts. With an exposure of 12 hours I obtained a photograph of the type of fig. 3. There was the direct image of the slit with the upper and lower portions in the same straight line, and in the upper half of the photograph where the rays had been exposed to the electric field there were two lines parallel to the slit, the deflexion from the direct image being in the direction in which electrons going through the slit would be deflected. There were no such lines in the lower part of the photograph where the rays had not been exposed to electric force. This seemed very convincing proof that the electric force did produce a gradient in the refractive index, and that the deflexion of electrons by electric force was due to the bending of the electronic waves, and not to the direct action of the electric force on the nucleus.

However, as the result of further experiments, I have come to the conclusion that the results obtained in the first photograph could not have been due to the cause we are considering; for, on trying the experiment with sulphur for the dielectric instead of mica, I got nothing but the direct image of the slit. There were no parallel bands in either the upper or lower portions of the photograph. Again, I got no evidence of such bands with paraffin-paper, with glass, or with quartz, varying the strength of the electric field from 5000 to 1200 volts. Nor on trying mica again could I get the effects I had observed with the mica plate I had used at first. Being unable to get the bands, I tried if I could get any evidence of any difference in intensity between the parts of the direct image of the slit formed by rays which had passed through the electric field and those which had not, using a plate of mica .3 mm. thick and a potential difference of 5500 volts. This, as the calculation given above shows, would drive all the harder of the γ -rays against the sides of the slit and thus prevent them from getting through. I got with an exposure of 12 hours a very clear and well-defined image of the slit, but I could not detect any difference between the upper part formed by γ -rays exposed to electric force and the lower part formed by rays which had not been exposed.

Thus the majority of the experiments favour the view that the electric force acts directly on the nucleus, and not by deflecting the waves*.

I am much indebted to Dr. Chadwick and Dr. Ellis for advice and information on radioactive experiments, to Mr. Crowe for the preparation of the radium emanation, and to my assistant, Mr. Everett, for help in the experiments.

* Since the above was in type I have seen a paper by A. Joffé (*Ann. der Phys.* lxxii. p. 461 (1923)) in which he describes some experiments which may modify this conclusion. He shows that when a plate of dielectric between electrodes is exposed to steady electric forces the drop in potential in many cases, though not in all, occurs quite close to the electrodes, and that the electric force may be very small, except in layers of almost molecular thickness next the electrodes. In my experiments it is possible that it was only in my first experiment that there was any considerable electric force between the plates, and that in the others it was confined to the immediate neighbourhood of the electrodes. I hope to make further experiments on this point.

where p_0 is the critical frequency ; hence, when $p > p_0$,

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CXXII. *Note on Raman Lines under High Dispersion.*
By Prof. R. W. WOOD*.

[Plate XXIX.]

SINCE the publication of my first paper on the Raman effect (Phil. Mag., Oct. 1928), I have photographed the spectra scattered by benzol and carbon tetrachloride with a 6-inch plane grating combined with a lens of 3-metres focus. Small portions of the spectra are reproduced on Plate XXIX. Fig. 2 shows the Raman line 4554·87 of benzene (wave-length determined from this photograph), together with the comparison spectrum of iron. The width of the line scattered by the liquid benzene excited by Hg 4358 is not much over half an Ångström unit in this case. Most of the other lines are wider (1 to 2·5 Å.). The one at 4618, excited by the mercury line 4046, which in my earlier photographs resembled a narrow band sharp and strong on the red side, turns out to be a strong line about 1 Å. wide, with a fainter line, 2·5 Å. wide, close to it on the violet side. The wave-lengths of the strongest lines determined from the grating photograph are as follows:—

4686·74		4554·87
4682·11		4525·0
4659·30		4476·0
4618·36		

Fig. 1 of Plate XXIX. shows a portion of the spectrum scattered by carbon tetrachloride, the three broad lines marked R being the strong triplet on the red side of Hg 4358 shown in the photograph accompanying the earlier paper. The scale of enlargement of this photograph is only about one half of that of the lower photograph, the width of the lines being about 2 Ångström units. One of the "ghosts" of the 4358 mercury line appears at the left of the photograph.

I feel disposed to think that such high resolving powers are quite unnecessary, owing to the considerable width of most of the lines. That some of them are as narrow as they are is very surprising. The range of frequencies comprised within the 4554·87 line (0·5 Å.U. wide) when translated into the frequency range of the corresponding

* Communicated by the Author.

infra-red absorption band gives a band enormously narrower than the band observed by Coblentz near $10\ \mu$.

Attention should be drawn to an error in the placing of the figures in my earlier paper. The mercury arc of fig. 2 was originally drawn just above and close to the water-cooled tube of fig. 1.

Johns Hopkins University,
Baltimore.

CXXIII. *The Hall Effect in Galena and Molybdenite.* By
C. W. HEAPS, Ph.D., Professor of Physics, The Rice
Institute, Houston, Texas*.

THE Hall coefficient in plates cast from molten lead sulphide has been found by van Aubel † to be negative and small compared with the coefficient for bismuth. A. W. Smith ‡, on the other hand, has found in a natural crystal of lead sulphide a value of -251 for this coefficient. L. L. Campbell § intimates that the discrepancy between the two results may be due to differences of crystalline structure.

The writer has performed some experiments on this substance and on molybdenite, and has come to the conclusion that impurities probably exert a big influence on the phenomenon in lead sulphide.

The apparatus was of the usual type, the Hall e.m.f. being balanced by a potentiometer. A Weiss electromagnet with pole-pieces 10 cm. in diameter and 1.315 cm. apart was used for producing the magnetic field. The field-strength was measured with a fluxmeter calibrated in the usual way by means of a standard of mutual inductance.

In determining the Hall coefficient observations of the e.m.f. were made for both directions of magnetic field and the mean taken as the correct result. Disturbing thermomagnetic effects were considered negligible for the following reason:—A magnetic field of about 10,000 gauss was allowed to act constantly on a specimen, the galvanometer circuit

* Communicated by the Author.

† E. van Aubel, *Phys. Zeits.* iv. p. 551 (1903).

‡ A. W. Smith, *Phys. Rev.* i. p. 339 (1913).

§ L. L. Campbell, 'Galvanomagnetic and Thermomagnetic Effects,'
p. 63.

being left open, and the primary current allowed to flow for about a minute. The primary current was then broken and immediately the galvanometer circuit closed. The resulting deflexion, which must have been due to residual thermoelectromotive forces, was, in the case of all the specimens examined, too small to affect materially the value of the Hall coefficient.

Lead Sulphide.—Four different specimens have been investigated. The first specimen was cut from a group of large cubic crystals of galena obtained from Joplin, Missouri. Cleavage planes were well developed in this specimen, but grinding and polishing revealed the presence of imperfections and irregularities due to tilting of small plane areas. The dimensions of the plate were $1.5 \times 0.8 \times 0.229$ cm., and its sides and edges were parallel to the respective natural cleavage planes of the crystal.

Electrical connexions were made by copper-plating and soldering with Wood's metal. The specific resistance of this specimen was found to be approximately 0.037 ohm-cm. The Hall e.m.f. was proportional to the magnetic field up to field-strengths of 12,000 gauss, and the average value of the Hall coefficient was found to be -108.3 .

The second specimen was cut from the same crystal group as the first. Its dimensions were $1.0 \times 0.407 \times 0.28$ cm., and the plate was cut so that its plane was approximately perpendicular to the trigonal axis of the crystal. The value of the Hall coefficient for this specimen was found to be the same, within experimental error, as for the first specimen. Thus the conclusion may be drawn that the Hall coefficient in galena is independent of the orientation of the crystal axis. A similar conclusion has been reached by Wold* for the cubic crystals of iron.

The third specimen was a crystal conglomerate made by fusing a mixture of lead and sulphur till chemical combination occurred. The specific resistance was 0.0012 and its Hall coefficient less than 0.008. It appears probable that some uncombined lead was present in the crystalline mass, otherwise the above results are difficult to explain.

The fourth specimen was from a very perfect crystal of unknown origin. Cleavage planes were mirror-like. Some slight difficulty was encountered in securing a flat plate because of the readiness of the crystal to split along any of three mutually perpendicular directions. The dimensions

* P. I. Wold, *Phys. Rev.* xxxi. p. 1116 (1928).

of the plate used were $0.197 \times 0.305 \times 0.831$ cm., and its specific resistance was 1.76 ohm-cm.

The Hall coefficient of this specimen was independent of field-strength up to 12,000 gauss, was positive in sign, and had the exceptionally large value +4802.

The remarkable difference in the Hall coefficients of the two crystals of galena examined is probably due to impurities. This mineral is known to have various impurities, such as silver, zinc, selenium, cadmium, bismuth, antimony, etc., and the proportions present appear to vary with the locality from which the crystals are secured. The specific gravity of specimen No. 1 was 7.2, that of No. 4 was 7.4. The first specimen was slightly pitted, and this fact may explain the difference of observed specific gravities. The resistivity of specimen No. 4 was much greater than that of No. 1. In view of Kapitza's work* on bismuth crystals we may expect a high resistance to be associated with transverse cleavage planes, such planes apparently having a tendency to produce incipient cracks. Under the blow-pipe each of the above crystals fused in similar fashion, yielding sulphurous fumes and a globule of metallic lead.

Molybdenite.—A thin plate, of dimensions $1.0 \times 2.0 \times 0.035$ cm., was cut from a foliated sheet of the mineral. Side arms 0.6 cm. long were left on the plate for the attachment of the Hall terminals. The resistance of the plate was 418 ohms. Using a primary current of 5 milliamperes the Hall e.m.f. was found to be proportional to the field up to 12,000 gauss, and the average of the Hall coefficient was —1907.

Adiabatic and Isothermal Coefficients.—Gottstein† has observed for the adiabatic Hall coefficient in molybdenite a value, $R_a = -3030$, from which he calculates by the formula of Gans‡ the isothermal coefficient of $R_i = -1520$. As the result of a number of experiments on molybdenite the writer has come to the conclusion that there is not much difference between the values of the two coefficients. The adiabatic coefficient is supposed to be obtained when the transverse temperature gradient, which results from interaction of magnetic field and electric current, is allowed to develop. This phenomenon, the Ettingshausen effect, is, according to

* Kapitza, Proc. Roy. Soc. cxix. p. 358 (1928).

† G. Gottstein, *Ann. d. Phys.* xlii. p. 1079 (1914).

‡ R. Gans, *Ann. d. Phys.* xx. p. 293 (1906).

Gottstein, quite large in molybdenite. In the present experiments, therefore, a transverse temperature gradient should be set up by the magnetic field. An appreciable time must be required for this gradient to reach its maximum value, so that if R_a is much larger than R_i then the apparent Hall effect should increase with the time after excitation of the magnet. In other words, the initial Hall effect is isothermal, and the adiabatic is approximated only after an appreciable time interval. If Gottstein's values for R_a and R_i are correct the apparent Hall effect should increase, while the temperature gradient is being set up, to about double its initial value. No such large increase could be observed in the present experiments with molybdenite, though it was specially sought for in the following way:—The adiabatic Hall e.m.f. was balanced carefully by adjusting the potentiometer. Switches in both the Hall circuit and the primary circuit were then opened and the specimen allowed to remain several minutes in the magnetic field without carrying any current. A uniform temperature was thus secured. The switch in the primary circuit was then closed and immediately afterwards (within a small fraction of a second) the switch in the Hall circuit. A small deflexion of the galvanometer resulted, and in about 15 seconds this deflexion became practically zero. From the value of the initial small deflexion it was calculated that the isothermal Hall coefficient was about 6 per cent. smaller than the adiabatic. Gottstein calculated it to be almost half as large.

The same type of experiment with galena showed the adiabatic and isothermal coefficients not to differ by more than 2 per cent. in this mineral.

Summary.—The chief points of interest which have been brought out are (1) galena and molybdenite crystals exhibit a very large Hall effect; (2) the magnitude of the Hall coefficient in the cubic crystal of galena does not appear to depend on the orientation of crystal axes; (3) impurities probably exert a very great influence on the Hall effect in lead sulphide, apparently even changing the coefficient from a large negative to a large positive value; (4) the difference between the adiabatic and the isothermal Hall effects appears to be small in these minerals. It is appreciable in molybdenite but by no means as great as Gottstein has calculated.

CXXIV. *Notice respecting New Book.*

A Comprehensive Treatise on Inorganic and Theoretical Chemistry.
By J. W. MELLOR, D.Sc., F.R.S. Vol. VIII. [Pp. x+1110,
with 156 diagrams.] (London: Longmans, Green & Co., 1928.
Price 63s. net.)

THE eighth of the thirteen volumes of which Dr. Mellor's 'Comprehensive Treatise' will consist is devoted to nitrogen and phosphorus. The treatment is along lines similar to that in the earlier volumes, which have received notice in these pages, and a detailed review is therefore unnecessary. It may be stated, however, that the latest volume to be issued fully maintains the high standard of its predecessors, in its completeness, in the care which has been devoted to the smallest detail, in the numerous diagrams and tabulation of data, and in the valuable lists of references to original publications. About one-eighth part of the whole volume is occupied by these references, and the fact that many bear the date 1927 is an indication that the author has included the results of the most recent original work. A detailed index, extending to 30 pages, increases the value of the volume for reference purposes. Dr. Mellor's 'Treatise' will undoubtedly become the standard work of reference on all matters pertaining to inorganic or theoretical chemistry.

EDITORIAL NOTE.

ACOUSTICS OF STRINGS STRUCK BY A HARD HAMMER.

IN reference to Messrs. Das and Datta's note on this subject in our September number (p. 479), Messrs. K. C. Kar and S. C. Laha have written stating that they do not consider that slipping at the bridge is the cause of the irregular and wide discrepancies between the observed and the calculated values of the amplitudes; and further, that their own observed value of the displacement at the centre agrees quite well with the value calculated from Kaufmann's theory. In regard to a paper by Prof. Raman and Dr. Banerji which is cited against them, they call attention to a paper by one of them in the Phil. Mag. for August 1928, where the results arrived at in that paper are shown to be incorrect. They also refer to their previous paper for their objections to the limits which Datta takes in his pressure integral. The unit of momentum in their own paper should have appeared as a "gramme-weight second."

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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END OF THE SIXTH VOLUME.

FIG. 3.



FIG. 4

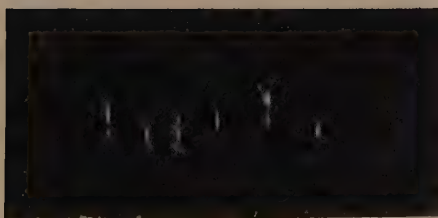


FIG. 5.

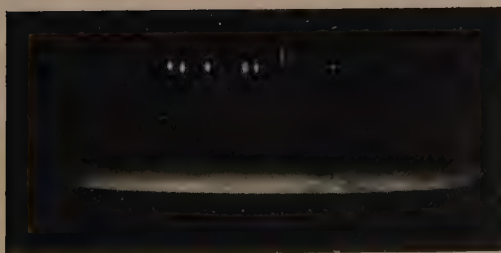


FIG. 6.



FIG. 7.

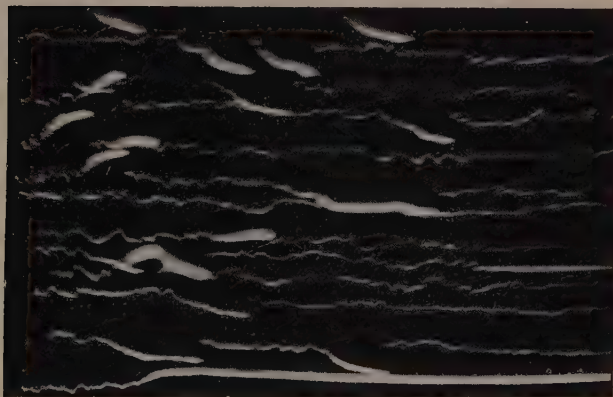


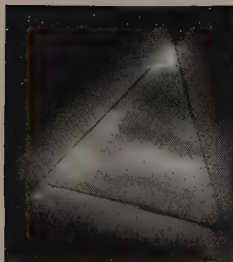
FIG. 8.

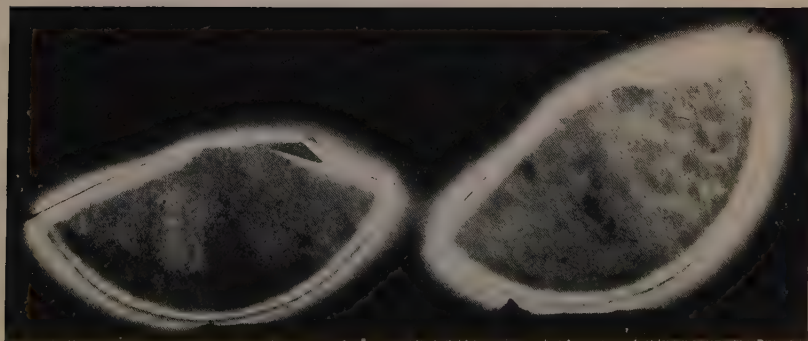
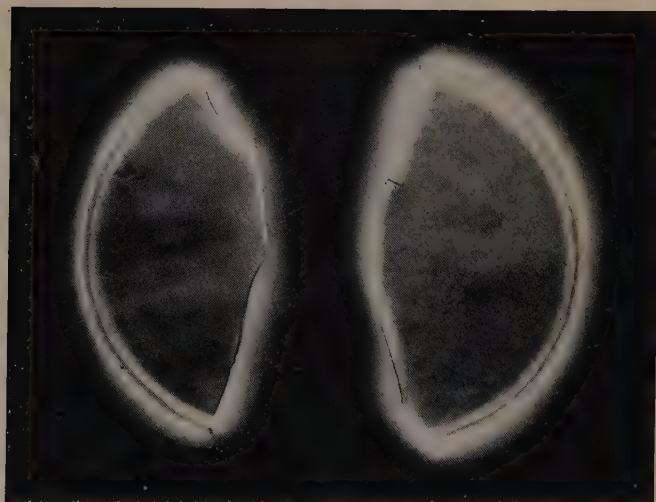


FIG. 1.



FIG. 2.





Prints of images obtained by placing certain pieces of fused quartz, activated by ultra-violet rays, upon a photographic plate for 12 hours.

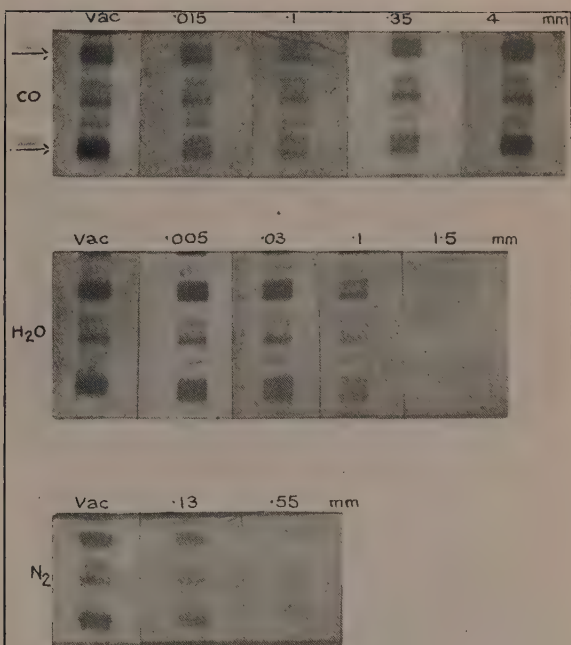


Fig 1.

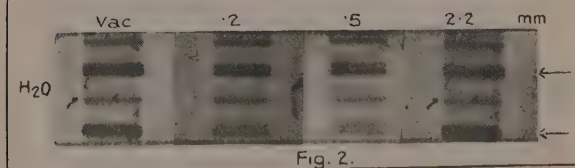
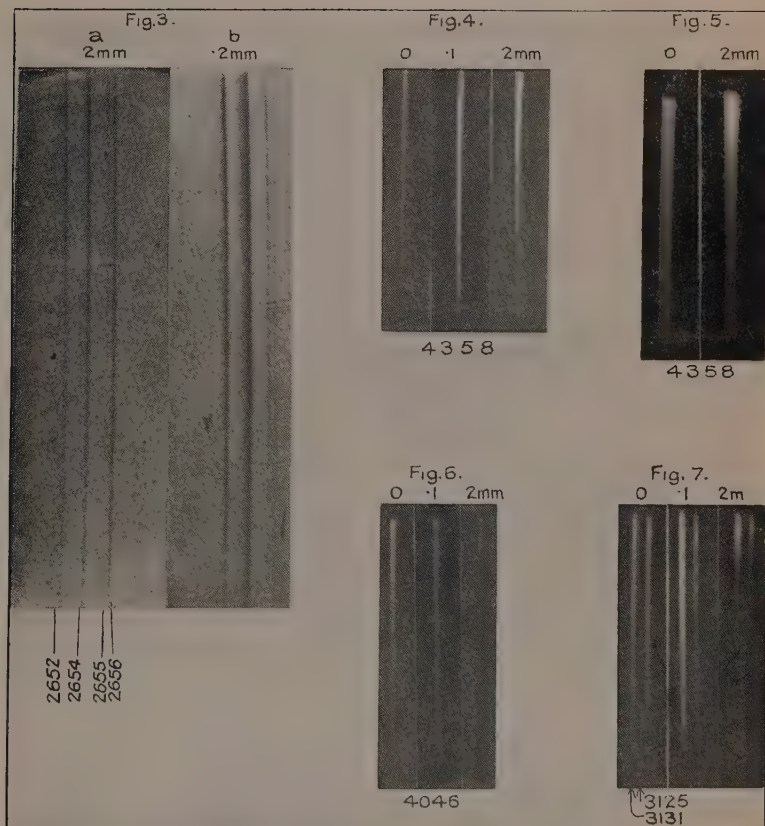
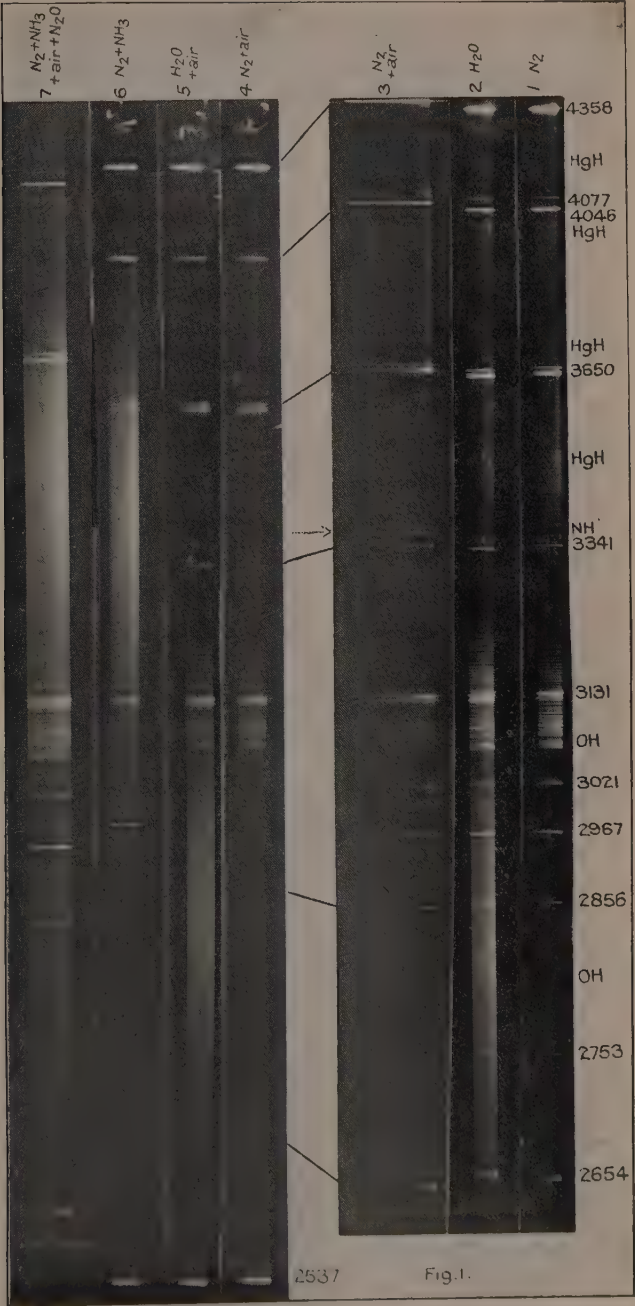


Fig. 2.





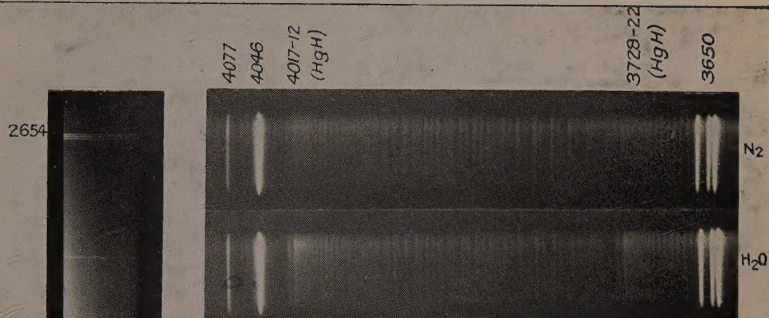


Fig. 2.

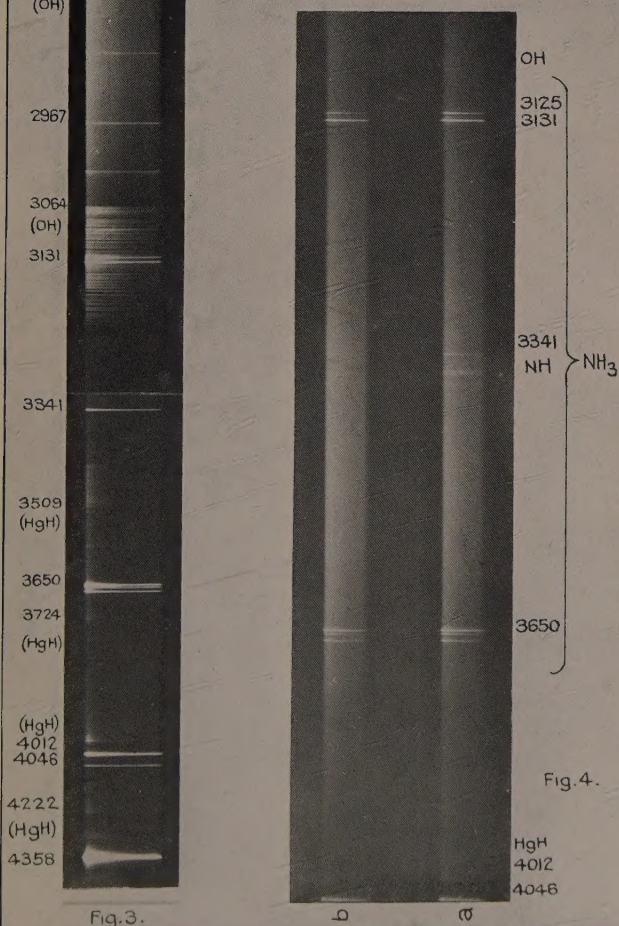
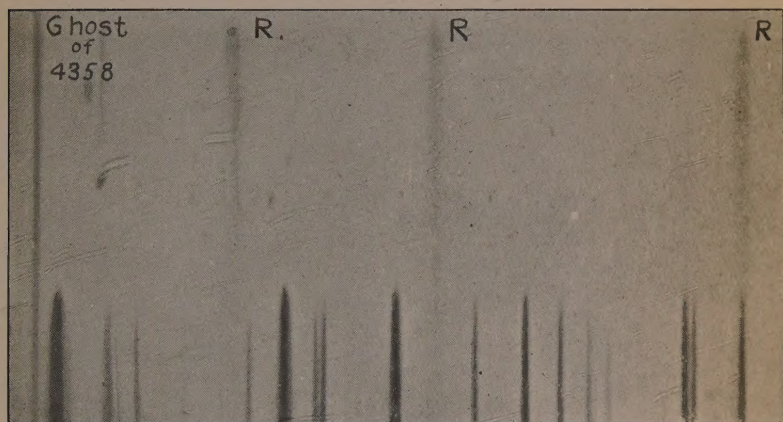


Fig. 3.

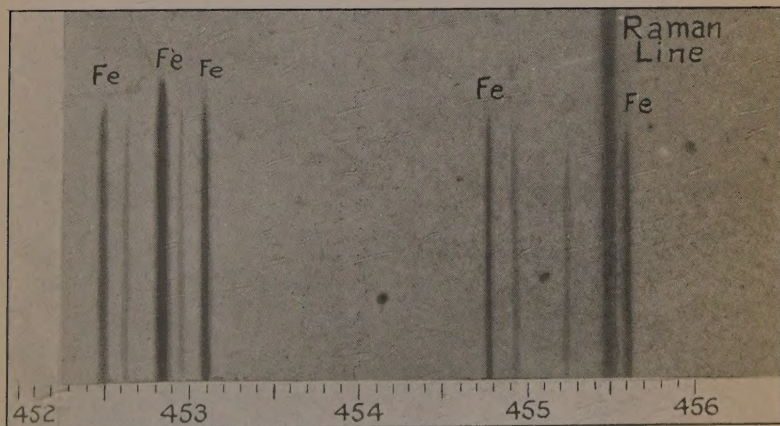
HgH
4012
4046

FIG. 1.



Carbon tetrachloride.

FIG. 2.



Benzene.

